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THE CHEMISTRY OF PETROLEUM DERIVATIVES

BY

CARLETON ELLIS

INDUSTRIAL RESEARCH CHEMIST

VOLUME II

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Contents

CHAPTER PAGE
1 Chemical Nature of Petroleum and Natural Gas. Pure Hydrocarbons from Petroleum . . . 7
2 Thermal Decomposition of Hydrocarbons . . . 49
3 Cracking Processes and Some of Their Products . . . 97
4 Production of Unsaturated Hydrocarbons by Pyrolysis . . . 148
5 Production of Aromatic Hydrocarbons by Pyrolysis of Petroleum Hydrocarbons . . . 177
6 Action of Aluminum Chloride on Hydrocarbons . . . 195
7 Production of Hydrogen and Carbon by Pyrolysis of Hydrocarbons . . . 218
8 The Carbon Black Industry. Deposition of Carbon from Flames . . . 235
9 Transformation of Hydrocarbons by Electrical and Other Special Forms of Energy . . . 253
10 Reactions of Hydrocarbons with Steam, Carbon Dioxide and Ammonia at High Temperatures . . . 269
11 Direct Hydration of Olefins to Alcohols . . . 282
12 Direct Esterification of Olefins with Mineral and Organic Acids . . . 298
13 Production of Ethyl Alcohol from Ethylene . . . 319
14 Reaction between Sulphuric Acid and Propene. Production of Isopropyl Alcohol . . . 356
15 Properties and Uses of Isopropyl Alcohol and Its Derivatives . . . 366
16 Production of Higher Secondary and Tertiary Alcohols. Reactions of Sulphuric Acid with Higher Homologues of Ethylene and Propene 385
17 Properties and Uses of Higher Secondary and Tertiary Alcohols Derived from Olefins . . . 399
18 Production, Properties and Uses of Ketones Derived from Alcohols and from Hydrocarbons . . . 419
19 Sulphur and Sulphur Compounds in Petroleum and Its Distillates. Their Occurrence, Chemical Properties and Possible Applications . . . 454
20 Reactions of Olefins with Halogens. Olefin Dihalides and Their Derivatives . . . 491
21 Production, Properties and Uses of Halohydrins Derived from Simple Olefins . . . 515
22 Production, Properties and Uses of Simple Glycols . . . 532
23 Production, Properties and Uses of Olefin Oxides and Their Derivatives 550
24 Miscellaneous Reactions of Olefins (I) . . . 591
25 Miscellaneous Reactions of Olefins (II) . . . 616
26 Polymerization of Monolefins and Diolefins. Synthetic Polymerization Products . . . 631
27 Some Important Reactions of Diolefins . . . 676
28 Important Reactions of Acetylene . . . 701
29 Halogenation of Methane. Properties and Uses of Halogen Derivatives 726
30 Halogenation of Methane Homologues. Properties and Uses of Halogen Derivatives . . . 740
31 Halogenation of Cycloparaffins . . . 760
32 Halogenation of Benzene and Its Immediate Homologues . . . 777
33 Production of Alcohols by Hydrolysis of Alkyl Halides. Production of Esters . . . 796

CHAPTER PAGE
34 MISCELLANEOUS REACTIONS OF HALOGEN DERIVATIVES OF PARAFFINS AND CYCLOPARAFFINS 804
35 EXTRACTION OF NITROGEN COMPOUNDS FROM PETROLEUM 831
36 OXIDATION OF PETROLEUM HYDROCARBONS. GENERAL CONSIDERATIONS . . . 843
37 OXIDATION OF METHANE AND ITS HOMOLOGUES 866
38 FORMALDEHYDE AND OTHER ALDEHYDES 877
39 OXIDATION OF UNSATURATED HYDROCARBONS 892
40 AUTOXIDATION OF PETROLEUM DISTILLATES. GUM FORMATION 905
41 OXIDATION OF AROMATIC HYDROCARBONS 942
42 PRODUCTION OF ACIDS FROM PETROLEUM HYDROCARBONS 962
43 OXIDATION OF PARAFFIN WAX 970
44 OXIDATION FROM THE STANDPOINT OF DETONATION 980
45 MISCELLANEOUS OXIDATION REACTIONS. ALCOHOLS, DENATURANTS AND OTHER PRODUCTS 1041
46 SULPHONATION OF PETROLEUM HYDROCARBONS. SULPHONIC ACIDS, DETERGENTS AND OTHER PRODUCTS 1064
47 CHEMICAL ACTION OF NITRIC ACID AND VARIOUS OTHER REAGENTS ON SATURATED HYDROCARBONS 1087
48 NAPHTHENIC ACIDS 1103
49 ANALYSIS OF NATURAL GAS AND CRACKING GAS 1121
50 ANALYSIS OF PETROLEUM DISTILLATES 1149
51 PETROLEUM ASPHALTS 1186
52 REDUCTION OF CARBON MONOXIDE TO HYDROCARBONS. THE KOGASIN SYNTHESIS AND SYNTHETIC PETROLEUM 1223
53 PETROLEUM HYDROCARBONS IN ANESTHESIA 1256
54 THERMODYNAMICS AND ITS APPLICATION TO PETROLEUM TECHNOLOGY . . 1270
NAME INDEX 1345
SUBJECT INDEX 1373

Preface

This volume serves to continue the subject matter of the earlier Chemistry of Petroleum Derivatives published in 1934. In some cases additional references to work published prior to that year have been included.

Little by little, as knowledge of the chemistry of various derivatives of petroleum expands, a comprehensive record of the work, other than that scattered information constituting the original papers, appears to be needed. This, then, is the purpose of the present volume.

The issuance of a book of the present size, so soon after the publication of the earlier volume, betokens to some extent the activity of investigators in this field. For this reason a revision of the 1934 volume was not attempted and the present publication is, as noted, essentially a continuation of the subject.

Since 1934 much material of importance to the petroleum chemist has appeared. Attention is especially directed to such chapters as those relating to sulphur (Chapter 19) and sulphonation (Chapter 46), dealing with utilization of by-products of refining; to polymerization (Chapter 26), a type of reaction applicable to the synthesis of motor fuels from gaseous hydrocarbons resulting from cracking or distillation operations; to detonation (Chapter 44), and to nitration (Chapter 47). In view of its growing importance to the petroleum industry a section treating the subject of thermodynamics has been included as Chapter 54.

A chapter has been added on the chemistry of asphalt and also one on a topic which perhaps at present is of less interest to the United States than to certain countries devoid of sources of petroleum; namely, to the production of hydrocarbons by treatment of carbon monoxide with hydrogen. Explanations or apologies, if any are needed, for discussing the subject here are that, despite our present abundant supplies of petroleum, there must needs come at some distant day a time when exhaustion of sources of petroleum will make inevitable a drastic survey of and search for other means of procuring liquid fuels. Numerous variations of carbon monoxide hydrogenation are known which result in a multiplicity of products. These modifications and others yet to be found may alter the aspect of petroleum chemistry. The search for new anesthetics has led many investigators to carry the hunt into the hydrocarbon field which serves to explain the presence of a new Chapter 53 on Petroleum Hydrocarbons in Anesthesia.

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Chapter 1

Chemical Nature of Petroleum and Natural Gas. Pure Hydrocarbons from Petroleum

Petroleum is found all over the world, although both the quantity and the character of the oil differ enormously from place to place and even from diverse strata at the same location.[1] Crude petroleum may vary from a light gasoline to a heavy pitch, and in some instances wells only yield gaseous petroleum in the form of natural gas. However, the main producing countries in the world are, in the order of decreasing production, United States, Russia, Venezuela, Persia and Rumania. In Table 1 are given details of the total world's production of petroleum for the years 1930 to 1935.

TABLE 1. *World Production of Petroleum, 1930-35, by Countries, in Thousands of Barrels.*

Country	1930	1931	1932	1933	1934	1935
United States	898,011	851,081	785,159	905,656	908,065	993,942
U.S.S.R.	125,555	162,842	154,367	154,840	174,318	176,688[a]
Sakhalin	1,805	2,734	2,631	2,338	2,881	(b)
Venezuela	136,669	116,613	116,541	117,720	136,103	149,113
Rumania	42,758	49,741	53,815	54,020	62,063	61,371
Iran	45,833	44,376	49,471	54,392	57,851	57,304
Netherland India	41,729	35,539	39,001	42,606	46,925	47,131
Mexico	39,530	33,039	32,805	34,001	38,172	40,235
Iraq	909	900	836	917	7,689	26,500
Columbia	20,346	18,237	16,414	13,158	17,341	17,595
Peru	12,449	10,089	9,899	13,257	16,314	17,067
Argentina	9,002	11,709	13,139	13,691	14,024	14,253
Trinidad	9,419	9,744	10,126	9,561	10,894	11,671
India, British	8,887	8,715	8,817	8,743	10,503	9,227
British Borneo (Sarawak and Brunei)	4,907	3,854	3,796	4,490	5,140	4,974
Poland	4,904	4,662	4,116	4,072	3,913	3,808
Germany	1,222	1,608	1,608	1,665	2,187	2,983
Japan (including Taiwan)	2,047	1,966	1,630	1,455	1,821	1,900
Ecuador	1,553	1,762	1,597	1,620	1,637	1,732
Canada	1,522	1,543	1,044	1,145	1,417	1,430
Egypt	1,996	2,038	1,895	1,663	1,546	1,295
Bahrein Island				31	285	1,265
France	523	527	530	562	557	535
Czechoslovakia	157	134	126	122	178	200
Bolivia	56	25	44	112	159	(b)
Italy	59	124	208	204	151	125[a]
Other countries	56	54	62	71	96	261
Total	1,411,904	1,373,656	1,309,677	1,442,112	1,522,230	1,642,605

[a] Approximate production.
(b) Data not available.

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[1] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934, 11.

[2] Minerals Yearbook (U. S. Bur. Mines), 1936, 702. *Cf.* A. Knapp, *Mineral Ind.*, 1935, 44, 433; *Chem. Abs.*, 1936, 30, 7825.

In the United States, which is still by far the most important producing country in the world, there was a three-fold increase of production for the period 1920-1934 over 1901-1919 despite reduction of 13.4 per cent in the number of wells drilled.[3] While the average production per well drilled has increased from 925 cubic meters (for 1857-1900) to 6128 cubic meters (for 1920-1934) largely as the result of improved technique, there has been an upward trend in the number of dry wells. This fact indicates the increasing difficulty of discovering new producing horizons in spite of improvements in drilling practice. The economic and political factors which have played a prominent role in directing the development of the petroleum industry in the United States and other countries have been examined by Leupold.[4]

Production of petroleum in the U.S.S.R. increased 515 per cent during the period 1920-1931 and was 11 per cent of the world's total in 1934. Leupold states that the situation in Russia is still inferior to that of other main producing countries and that considerable waste of petroleum resources occurs. Russian exports of petroleum have decreased considerably since 1932 as a result of unfavorable conditions of production and refining, increased domestic consumption and economic and political difficulties.

The Venezuelan oil industry is largely controlled by certain international groups, particularly the Standard Oil subsidiaries, which, in view of the possible diminution of U.S.A. oil reserves, have striven to secure extra supplies in other regions.

In view of the enormous, and increasing, production of crude petroleum, the question of the total available resources of the United States is of major importance. Although there is always the possibility of ultimate exhaustion of petroleum resources, past estimates of such have invariably proven far too low, largely as a result of improved drilling technique, especially that of deeper wells. In the period 1922-1934, the crude oil reserves of the United States have increased from 5000 million barrels to over 13,000 million barrels in spite of the fact that production during that period totaled 9782 million barrels. In the face of a constantly increasing consumption of petroleum products, the visible supplies in the United States, obtainable by methods within the range of present production costs, have increased from 11 years' supply in 1922 to 15¼ years' supply at the rate of consumption at the end of 1933.[5] It must be remembered, also, that the 13,250 million barrels of producible oil estimated to have existed in the United States at the beginning of 1934 represent but a fraction of the ultimate total oil reserves of that country. There are still practically no completely exhausted oil areas in the United States, and the development of deeper drilling is opening up oil-bearing strata which are much more prolific than the shallower sands previously exploited. In the light of evidence available in 1934, the estimate that no shortage of oil will occur for at least 25 years[6] does not seem unduly optimistic. However, a more pessimistic view of the situation has been adopted by Brooks.[6a] He believes that the statement of oil reserves in terms of a number of years is misleading as indicating that no concern need be felt until the end of that period; whereas, fresh supplies of considerable magnitude will be needed in a relatively shorter period if the present production level is to be maintained. Brooks considers it probable that at some future period the cost of production of petroleum will tend to increase, and a point will be reached when certain substitutes (including shale oil or oil from the hydrogenation of coal) will begin to compete and check the rising price of natural oil.[7]

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[3] E. Leupold, *Bol. Inform. Petroleras (Buenos Aires)*, 1935, 12 (136), 17; *J. Inst. Pet. Tech.*, 1936, 22, 169A.

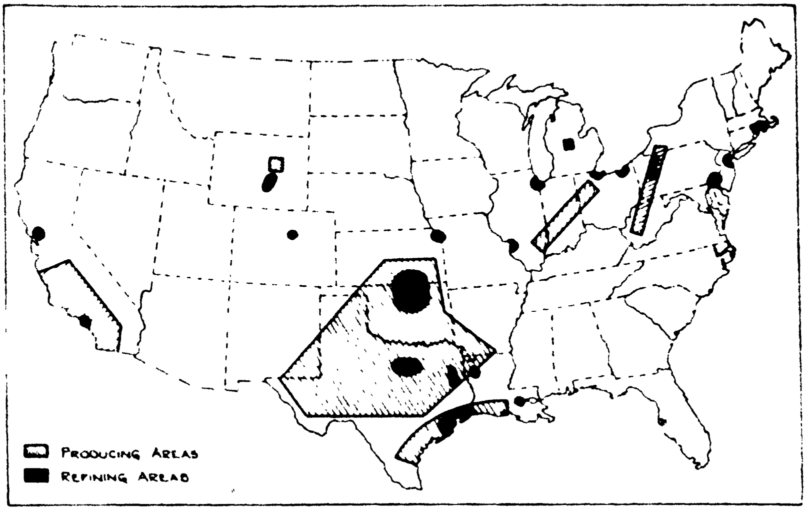
[4] E. Leupold, *loc. cit.*

[5] S. Gill, "Report on the Petroleum Industry of the United States," Nov. 15, 1934.

[6] Standard Oil of California Bulletin, 1935, 23 (7), 16. See also, H. W. Hoots, *Bull. Am. Assoc. Petroleum Geol.*, 1936, 20, 939; *J. Inst. Pet. Tech.*, 1936, 22, 423A.

[6a] B. T. Brooks, *The Chemist*, 1935, 12, 333.

Improvements in operating technique have rendered possible the drilling of wells as deep as 11,380 feet, thus making available oil reservoirs previously inaccessible. The elimination of crooked-hole drilling has been an important factor in reducing waste. Other improvements include deep-well pumping, rendering possible the recovery of oil from depths previously considered to be beyond the reach of the pump, as well as the restoration and maintenance of pressure on oil sands with stripped natural gas or air.[8] Older methods are shooting with nitroglycerin and the application of vacuum to wells. Flooding oil sands with water is also effective in some fields in increasing production more than tenfold.[9] An interesting procedure applicable to limestone formations consists in pumping aqueous hydrochloric acid (in the presence of an inhibitor to minimize pipe-line corrosion) into the sand to increase porosity. This method, which is usually termed acidation, caused an average increase in production (for approximately 3000 acidized wells) of about 448 per cent. Furthermore, a number of wells previously abandoned as non-profitable have been rendered productive in this manner.[10]



Courtesy Industrial and Engineering Chemistry

FIG. 1.—Most Important Producing Areas and Refining Centers in 1935. (J. B. Hill)

The most important producing areas and refining centers in the United States[11] in 1935 are indicated in Fig. 1. Table 2 shows the consumption of various petroleum products throughout the world in 1935.[12]

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[7] See also L. C. Snider and B. T. Brooks, "Petroleum Shortage and Its Alleviation." The Chemical Foundation, New York; *Chem. Abs.*, 1936, **30**, 1986; *Rubber Age*, 1936, **38**, 217.

[8] In connection with increasing oil-well production by repressuring with natural gas, E. A. Bertram and W. N. Lacey (*Ind. Eng. Chem.*, 1936, **28**, 316; *Brit. Chem. Abs.* **B**, 1936, 435; *Chem. Abs.*, 1936, **30**, 2830; *J. Inst. Pet. Tech.*, 1936, **22**, 252A) measured the rate of solution of methane in oils filling the spaces between sand grains. They report the presence of the latter did not introduce surface effects due to the presence of large amounts of sand oil interface which might assist the solution process.

[9] G. Egloff, *Ind. Eng. Chem.*, 1935, **27**, 648; *Chem. Abs.*, 1935, **29**, 4556; *J. Inst. Pet. Tech.*, 1935, **21**, 286A.

[10] The chemically controlled acidation of oil wells has been described by S. W. Putnam and W. A. Fry, *Ind. Eng. Chem.*, 1934, **26**, 921; *Chem. Abs.*, 1934, **28**, 6987; *Brit. Chem. Abs.* **B**, 1934, 1044; *J. Inst. Pet. Tech.*, 1934, **20**, 555A.

[11] J. B. Hill, *Ind. Eng. Chem.*, 1935, **27**, 519; *Chem. Abs.*, 1935, **29**, 3813.

TABLE 2.—*World Consumption of Petroleum Products in 1935.*

(Thousands of Barrels)

	Motor Fuel	Kerosene	Gas and Fuel Oil	Lubricants	Miscellaneous	Total
United States	435,300	47,500	346,400	19,900	126,900	976,000
Russia	13,565	28,555	56,112	8,150	16,888	123,270
United Kingdom	37,454	6,015	25,894	2,692	2,121	74,176
France	22,200	1,890	14,210	2,110	2,000	42,610
Canada	16,650	1,750	14,700	830	1,690	35,620
Germany	15,810	1,010	8,850	2,660	2,010	30,340
Argentina	5,710	1,180	13,700	320	850	21,760
Japan	7,122	1,130	13,800	1,602	1,220	24,874
Mexico	2,100	610	11,400	160	2,580	16,850
Rumania	790	1,380	11,900	220	1,700	15,990
British India	2,300	6,200	3,700	950	1,080	14,230
Italy	4,563	1,502	7,600	615	1,660	15,940
Dutch East Indies	1,600	2,390	4,900	540	1,480	10,910
Australia	6,600	1,090	2,990	400	500	11,580
Dutch West Indies	180	25	11,800	30	2,400	14,435
Holland	3,410	1,680	2,110	400	810	8,410
Persia	710	1,380	3,600	610	1,510	7,810
China	1,034	2,666	3,010	281	111	7,102
Venezuela	520	22	900	28	5,200	6,670
Brazil	2,400	750	3,200	170	50	6,570
Others	41,845	17,431	59,928	4,608	6,673	127,432
Total	621,863	126,156	617,704	47,429	179,433	1,592,585

NOMENCLATURE

As an aid to understanding the many terms applied to petroleum or its distillates, Table 3 (page 11) includes the synonyms often employed in the United States, Germany, England and France.[13]

GENERAL CHEMICAL CHARACTER OF CRUDE PETROLEUM

Crude oil consists essentially of a complex mixture of liquid and solid hydrocarbons, often containing dissolved gaseous hydrocarbons, together with smaller proportions of organic sulphur and nitrogen compounds. Oxygen-containing substances which may be present include organic acids (so-called naphthenic acids), small quantities of phenols and dissolved carbon dioxide. The carboxylic acids appear to be mainly derivatives of mono- and bicyclic naphthene (or cycloparaffinic) hydrocarbons, particularly cyclopentanes, although the higher straight-chain fatty acids have also been found.[14] As it issues from the well, crude petroleum is often associated with much water, usually containing dissolved inorganic materials. In some cases, relatively stable emulsions of oil and water are obtained. To reduce the aqueous content of the crude oil to pipe-line specification of 2 per cent or less, it is necessary to break such emulsions. The action of heat with or without the application of pressure is often employed, although chemical

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[12] V. R. Garfias and R. V. Whetsel, *Nat. Pet. News*, 1936, **28** (9), 20. *Cf. Petroleum Z.*, 1936, **32** (44), 21.

[13] R. Schwarz, *Proc. World Petroleum Congr.*, 1933, **2**, 897; *Chem. Abs.*, 1934, **28**, 4869. This reference also gives the synonyms of similar words in about twenty languages.

[14] See Chapter 48. Also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

TABLE 3.—*Synonyms for Various Petroleum Distillates.*

In U.S.A.	German	English	French
Petroleum Crude oil Crude	Rohöl Erdöl, roh Naphtha, roh	Petroleum Crude oil	Huile brute Pétrole brute
Light gasoline	Petrol-Äther Gasolin Leichtbenzin	Light petrol	Essence volatile
Benzine	Benzin Rohbenzin	Benzine	Benzine
Gasoline Gas (popular)	Benzin Motorenbenzin	Petrol Motor spirit	Essence Essence moteur
Naphtha Solvent naphtha	Lösungsbenzin Test-Benzin Wasch-Benzin Solvent-Naphtha	White spirit Solvent naphtha	White spirit Solventnaphta
Kerosene	Petroleum Leuchtöl Solarol Traktoren-Brennstoff	Kerosine Paraffin oil Paraffin	Essence à pétrole Pétrole lampant
Gas oil Diesel oil	Gasöl Dieselöl Schwerol Rohöl (fälshlich)	Gas oil Diesel oil	Gas oil Huile pour Diesel
Fuel oil Furnace oil	Heizöl, Mazut Pakura	Fuel oil	Fuel oil Mazout
Benzene	Benzol Reinbenzol	Benzene	Benzole
Benzole	Benzol Motoren-Benzol	Benzole	Benzole
Spirit	Alkohol, Sprit Äthylalkohol	Alcoholic spirit	Benzole moteur Alcohol

or electrical precipitation is also used.[15] The inorganic materials which may be present in crude oil are considered later.

It is interesting to note that, although the chemical nature of many sulphur compounds and some nitrogen bases in distillates has been clearly established, little is known of the character of such compounds in crude undistilled petroleum. Although, for example, certain Californian petroleums of relatively high nitrogen content contain no basic materials capable of extraction with aqueous acids, their distillates furnish appreciable quantities of such bases. This has been attributed to the breaking down, or partial decomposition, of more complex nitrogen-containing bodies at distillation temperatures.[16] Similar observations have been made in the case of the sulphur and oxygenated organic constituents. Thus, Pyhälä[17] showed that some fractions derived from Russian petroleum contained about 12 times as much naphthenic acids as the undistilled crude oils. Whereas relatively simple organic sulphur compounds are found in distillates, and particularly cracked distillates, these are not present in the parent petroleum. In this connection, Kewley[18] reports that crudes, relatively rich in sulphur compounds, yield about 35 per cent of sweet-smelling liquids free from corrosive sulphur, if vacuum distilled below 140°C. At this temperature, however, decomposition of some of the unstable thio-compounds in certain crudes begins to occur. It is suggested by von Braun[19] that the nitrogen bases are formed by decomposition of albuminous substances in the crude. Under such circumstances no correlation appears possible between the composition of the sulphur- and nitrogen-containing bodies of distillates and the character of the crude oil from which they are derived.

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[15] Some reagents for breaking oil and water emulsions are discussed in Chapters 46 and 48.

[16] E. J. Poth, W. A. Schulze, W. A. King, W. C. Thompson, W. M. Slagle, W. W. Floyd and J. R. Bailey, *J.A.C.S.*, 1930, **52**, 1239; *Chem. Abs.*, 1930, **24**, 1864; *Brit. Chem. Abs.* **A**, 1930, 788.

[17] E. Pyhälä, *Chem.-Ztg.*, 1933, **57**, 273; *Brit. Chem. Abs.* **B**, 1933, 452; *Chem. Abs.* 1933, **27**, 4912.

[18] J. Kewley, discussion in article by B. T. Brooks, *J. Inst. Pet. Tech.*, 1934, **20**, 177, 276A; *Chem. Abs.*, 1934, **28**, 3694; *Brit. Chem. Abs.* **A**, 1934, 507.

The important observation has been made by Treibs[20] that crude petroleums, as well as asphalts and oil-shales, contain detectable amounts of porphyrins, presumably derived from chlorophyll-containing materials. The presence of complex compounds of porphyrins with vanadium or bivalent iron in petroleum and bituminous extracts has also been demonstrated by Treibs.[21] It is significant that the California petroleums which yield fractions containing nitrogen bases are also relatively rich in chlorophyll porphyrins. The presence of optically active constituents in crude petroleum has long been known.[22]

CLASSIFICATION OF PETROLEUMS

The older methods of classification of crude oils into various basic types has for some time been considered inadequate and a new scheme, in which nine possible types of petroleum are recognized, has been outlined by Lane and Garton.[23] The basis of the new arrangement is the boiling point-gravity curve of the sample under investigation. Distillation up to 275°C. is carried out at atmospheric pressure and then continued at 40 mm. pressure. The observed gravities of two key fractions, namely, (1) that boiling at 250-275°C. at atmospheric pressure, and (2) that boiling at 275-300°C. at 40 mm. absolute pressure, are used to evaluate the base of the crude oil. Thus, if the A.P.I. gravity of the first key fraction is 40° or lighter, the lower-boiling fractions would fall in a paraffinic class. If it is 33° or heavier, they are naphthenic. If it is between 40 and 33°, lighter fractions are intermediate in type. Should the A.P.I. gravity of the second key fraction be 30° or more, then the higher-boiling portions are considered as paraffinic. When the gravity of this second fraction is 20° A.P.I. or less, then the higher-boiling distillates are assumed to be naphthenic. On the other hand, a gravity of 20 to 30° A.P.I. denotes the heavier portions to be intermediate. The following types are distinguished.

1. Paraffin base: distillates paraffinic throughout.
2. Paraffin-intermediate base: light fractions paraffinic, heavy fractions intermediate.
3. Intermediate-paraffin base: light fractions intermediate, heavy fractions paraffinic.
4. Intermediate base: distillates intermediate throughout.
5. Intermediate-naphthene base: light fractions intermediate, heavy fractions naphthenic.
6. Naphthene-intermediate base: light fractions naphthenic, heavy fractions intermediate.
7. Naphthenic base: distillates naphthenic throughout.

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[19] J. von Braun, *Petroleum Z.*, 1932, **28** (50), 1; *Chem. Abs.*, 1933, **27**, 1491.

[20] A. Treibs, *Ann.*, 1934, 510, 42; *Brit. Chem. Abs.* **A**, 1934, 629; *Chem. Abs.*, 1934, **28**, 7211.

[21] A. Treibs, *Ann.*, 1935, 517, 172; *Brit. Chem. Abs.* **A**, 1935, 727; *Chem. Abs.*, 1935, **29**, 4708.

[22] P. Walden, *Chem.-Ztg.*, 1906, **30**, 391; *J.C.S.*, 1906, **90** (2), 368.

[23] E. C. Lane and E. L. Garton, *U. S. Bureau of Mines Rept. Invest.* 3279, 1935; *Brit. Chem. Abs.* **B**, 1935, 1081; *Petr. Times*, 1935, **34**, 429, 455; *Chem. Abs.*, 1935, **29**, 7626; *J. Inst. Pet. Tech.*, 1936, **22**, 16A.

8. Paraffin-naphthene base: light fractions paraffinic, heavy fractions naphthenic.
9. Naphthene-paraffin base: light fractions naphthenic, heavy fractions paraffinic.

In another scheme of classification elaborated by Sakhanov and Virabyantz[24] and based on the relative proportions of paraffin, naphthene and aromatic hydrocarbons in various fractions, the following six types are defined:

1. Methane base.
2. Naphthene base.
3. Methane-naphthene base.
4. Aromatic base.
5. Methane-naphthene-aromatic base.
6. Naphthene-aromatic base.

HYDROCARBON CONSTITUENTS

As previously mentioned, the preponderating constituents of all petroleums are hydrocarbons. These may vary from gases or volatile liquids to heavy pitches, and consist of paraffins, naphthenes, aromatics, and polynuclear naphthenes and polynuclear aromatics. Unsaturated hydrocarbons, such as olefins, apparently are not found in undistilled crude oils. A very large number of chemical individuals are usually present even in a distillate of relatively narrow boiling range. Furthermore, crude oils display great variations in distillation data and general physical properties as well as in the chemical compositions of similar fractions.

The widely different proportions of paraffins, naphthenes, aromatic hydrocarbons, wax and asphalt in some petroleums, as reported by Stadnikoff,[25] are summarized in Table 4. Paraffin hydrocarbons are the sole constituents of the gaseous and volatile liquid portions of crude petroleums, at least up to and including those components having four carbon atoms per molecule. In many instances, such aliphatic compounds are present in large amounts in all fractions. The higher members are solids and are found as paraffin wax, petrolatum and ceresin in the higher-boiling fractions of many crude oils.

TABLE 4.—*Average Composition of Typical Petroleums.*

Type of Crude	Solid Paraffin Per Cent	Resins and Asphaltene Per Cent	Composition of 250-300°C. Fraction			Specific Gravity of Residue Boiling Over 300°C.
			Paraffins	Naphthenes	Aromatics	
Paraffin	1.5-10	0-6	46-61	22-32	12-25	0.897-0.929
Paraffin-naphthene	1-6	0-6	42-45	38-39	16-20	0.897-0.908
Naphthene	Trace	0-6	15-26	61-76	8-13	0.895-0.912
Aromatic-naphthene	0.5-1	0-10	27-35	36-47	26-33	0.921-0.949
Aromatic-paraffin-naphthene	0-0.5	0-20	0-8	57-78	20-35	0.950-0.970

The simple naphthene hydrocarbons in petroleum belong to the cyclopentane and cyclohexane series, while polycylic hydrocarbons of both types probably exist in the higher fractions. The relative proportions of cyclopentanes and cyclohexanes in various Russian straight-run gasolines have been determined by Sakhanov, Doladugin and Egorova.[26] All the crude oils examined, with a single exception, had a maximum content of cyclohexane hydrocarbons in the fraction boiling at 95-122°C.

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[24] A. N. Sakhanov and R. A. Virabyantz, *Erdöl u. Teer*, 1933, **9**, 170, 187, 202, 220; *Chem. Abs.*, 1934, **28**, 295.

[25] G. L. Stadnikoff, *Schriften aus dem Gebiet der Brennstoff-Geologie*, 1930, No. 5-6, 213; *Chem. Abs.*, 1931, **25**, 1472. See also F. D. Rossini, *Proc. Am. Petroleum Inst., 5th Mid-Year Meeting*, 1936, Sect. III, **16**, 63; *Refiner*, 1935, **14**, 266; *Oil & Gas J.*, 1935, **34** (6), 41; *Chem. Abs.*, 1937, **31**, 530.

[26] A. N. Sakhanov, A. I. Doladugin and I. M. Egorova, *Gosudarstvennoe Nauch.-Tekh. Izdatelstvo Moscow-Petrograd*, **1931**, 175; *Chem. Abs.*, 1934, **28**, 297.

A large amount of data has been collected concerning the hydrocarbons found in petroleum and its refined products. The melting points and boiling points of a number of paraffin hydrocarbons are shown in Table 5. Physical constants of

TABLE 5.—*Some Physical Constants of* n-*Paraffin Hydrocarbons.* [33]

Name of Hydrocarbon	Number of Carbon Atoms	Mol. Weight	Melting Point °C.	Boiling Point, °C.
Methane	1	16.03	− 184	− 161.4
Ethane	2	30.05	− 172.0	− 88.3
Propane	3	44.06	− 189.9	− 44.5
Butane	4	58.08	− 135.0	0.6
Pentane	5	72.09	− 131.5	36.2
Hexane	6	86.11	− 94.3	69.0
Heptane	7	100.12	− 90.0	98.4
Octane	8	114.14	− 56.5	124.6
Nonane	9	128.15	− 51	150.6
Decane	10	142.17	− 32.0	174
Undecane	11	156.18	− 26.5	197
Dodecane	12	170.20	− 12	216
Tridecane	13	184.22	− 6.2	234
Tetradecane	14	198.23	5.5	252.5
Pentadecane	15	212.25	10	270.5
Hexadecane	16	226.26	20	287.5
Heptadecane	17	240.28	22.5	303
Octadecane	18	254.29	28	317
Nondecane	19	268.31	32	330
Eicosane	20	282.32	38	205 (15 mm.)
Heneicosane	21	296.34	40.4	215 (15 mm.)
Docosane	22	310.35	44.4	224.5 (15 mm.)
Tricosane	23	324.37	47.7	320.7
Tetracosane	24	338.39	54	324.1
Pentacosane	25	352.40	54	284 (40 mm.)
Hexacosane	26	366.42	60	296 (40 mm.)
Heptacosane	27	380.43	59.5	270 (15 mm.)
Octacosane	28	394.45	65	318 (40 mm.)
Nonacosane	29	408.46	63.6	348 (40 mm.)
Triacontane	30	422.48	70	235 (1.0 mm.)
Hentriacontane	31	436.49	68.1	302 (15 mm.)
Dotriacontane	32	450.51	75	310 (15 mm.)
Tritriacontane	33	464.52		
Tetratriacontane	34	478.54	76.5	255 (1.0 mm.)
Pentatriacontane	35	492.55	74.7	331 (15 mm.)
Hexatriacontane	36	506.57	76.5	265 (1.0 mm.)

propane are given by Cox,[27] Beattie, Poffenberger and Hadlock,[28] Lacey and Sage,[29] Hicks-Bruun and Bruun[30] and Justi.[31] Beall[32] has collected some of the available data for pentane; while the physical properties of the isomeric hexanes and information concerning isomeric octanes are to be found in the work of

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[27] E. R. Cox, *Oil & Gas J.*, 1935, **33** (33), 16; *J. Inst. Pet. Tech.*, 1935, **21**, 85A.

[28] J. A. Beattie, N. Poffenberger and C. Hadlock, *J. Chem. Physics*, 1935, **3**, 96; *Chem. Abs.*, 1935, **29**, 2044; *Brit. Chem. Abs.* **A**, 1935, 437.

[29] W. N. Lacey and B. H. Sage, *Oil & Gas. J.*, 1935, **33** (39), 49; *J. Inst. Pet. Tech.*, 1935, **21**, 203A.

[30] M. M. Hicks-Bruun and I. H Bruun, *J.A C.S.*, 1936, **58**, 810; *Chem. Abs.*, 1936, **30**, 5086; *J. Inst. Pet. Tech.*, 1936, **22**, 297A; *Brit Chem. Abs.* **A**, 1936, 787.

[31] E. Justi, *Z. Ver. deut. Ing.*, 1936, **80**, 103; *Brit. Chem. Abs.* **B**, 1936, 439; *Chem. Abs.*, 1936, **30**, 7097.

[32] I. N. Beall, *Refiner*, 1935, **14**, 588; *Chem. Abs.*, 1936, **30**, 2817.

[33] Values from "International Critical Tables," McGraw-Hill Book Co., Inc., New York and London, 1926, Volume I. High molecular weight paraffin hydrocarbons have been isolated in the products obtained by the Kogasin synthesis. For their physical properties, such as melting points, see Chapter 52.

Maman[34] and Whitmore and Laughlin,[35] respectively. The boiling points of the normal paraffin hydrocarbons are correlated by Cox[36] and Wakeman.[37] Calingaert and Hladky[38] summarized the data on the molecular volumes of the paraffin hydrocarbons. The change in ultraviolet absorption resulting from the alteration of mineral oils, and the rotary dispersion of a number of oils have been studied.[38a] The heats of combustion of ethane, propane, butane and pentane have been determined by Rossini[39] who later made a similar determination for isobutane.[40] Specific heats of pure liquid hydrocarbons and petroleum fractions are reviewed by Gaucher,[41] and the total heats of pentane and paraffinic naphtha under pressure have been determined by Pattee and Brown.[42] Physical properties of a number of higher paraffin hydrocarbons (C_{20}-C_{40}) have been determined by Ivanovszky.[43] Phase equilibria in various hydrocarbon systems, including specific heat measurements, have been studied by Lacey and his collaborators.[44] The viscosity of solutions of the higher paraffins have been measured by Staudinger and Staiger[45] and by Meyer and van der Wijk.[46] Sage, Sherborne and Lacey[47] determined the viscosities of solutions of ethane and *n*-butane in crystal oil.[48] Measurements of the boiling points and ultraviolet absorption of cyclopropane and propene have been made by Ashdown, Harris and Armstrong.[49] The density of liquid propene has been ascertained by Pall and Maass.[50] Some data concerning methyl nonanes has been obtained by Calingaert and Soroos;[51] and the experiments of Kassel[52] indicate the values for the vapor pressures of the xylenes and mesitylene. Several properties of series of hydrocarbons have been contributed

[34] Maman, *Compt. rend.*, 1934, **198**, 1323; *Chem. Abs.*, 1934, **28**, 3377; *Brit. Chem. Abs.* **A**, 1934, 629.

[35] F. C. Whitmore and K. C. Laughlin, *J.A.C.S.*, 1933, **55**, 5056; *Brit. Chem. Abs.* **A**, 1934, 168. *Chem. Abs.*, 1934, **28**, 737.

[36] E. R. Cox, *Ind. Eng. Chem.*, 1935, **27**, 1423; *Chem. Abs.*, 1936, **30**, 1277; *J. Inst. Pet. Tech.* 1936, **22**, 44A.

[37] R. L. Wakeman, *Rec. trav. chim.*, 1934, **53**, 832; *J. Inst. Pet. Tech.*, 1935, **21**, 15A; *Brit. Chem. Abs.* **A**, 1934, 950, *Chem. Abs.*, 1934, **28**, 6039.

[38] G. Calingaert and J. W. Hladky, *J.A.C.S.*, 1936, **58**, 153; *Chem. Abs.*, 1936, **30**, 1733; *J. Inst. Pet. Tech.*, 1936, **22**, 201A. V. G. Aranda, *Anales soc. españ. fís. quím.*, 1936, **34**, 513; *Chem. Abs.*, 1936, **30**, 6321; *Brit. Chem. Abs.* **B**, 1936, 1096.

[38a] E. Vellinger and A. Klinkenberg, *Ann. combustibles liquides*, 1935, **10**, 79, *Chem. Abs.*, 1935, **29**, 3815. E. Vellinger, *Chim. et ind.*, **1929**, Special No., 268; *Chem. Abs.*, 1929, **23**, 3801.

[39] F. D. Rossini, *J. Res. Nat. Bur. Standards*, 1934, **12**, 735; *Chem. Abs.*, 1934, **28**, 4974; *Brit. Chem. Abs.* **A**, 1934, 966; *J. Inst. Pet. Tech.*, 1934, **20**, 523A.

[40] F. D. Rossini, *J. Res. Nat. Bur. Standards*, 1935, **15**, 357; *Brit. Chem. Abs.* **A**, 1936, 291. *Chem. Abs.*, 1936, **30**, 674; *J. Inst. Pet. Tech.*, 1936, **22**, 86A.

[41] L. P. Gaucher, *Ind. Eng. Chem.*, 1935, **27**, 57; *Brit. Chem. Abs.* **A**, 1935, 289; *J. Inst. Pet. Tech.*, 1935, **21**, 85A; *Chem. Abs.* 1935, **29**, 1972.

[42] E. C. Pattee and G. G. Brown, *Ind. Eng. Chem.*, 1934, **26**, 511; *Chem. Abs.*, 1934, **28**, 4876, *Brit. Chem. Abs.* **B**, 1934, 567; *J. Inst. Pet. Tech.*, 1934, **20**, 400A.

[43] L. Ivanovszky, *Petroleum Z.*, 1934, **30** (42), 1; *Brit. Chem. Abs.* **A**, 1934, 1300; *Chem. Abs.*, 1935, **29**, 2715; *J. Inst. Pet. Tech.*, 1934, **20**, 608A.

[44] W. N. Lacey and others, *Ind. Eng. Chem.*, 1934, **26**, 103, 214, 652, 874, 1218; 1935, **27**, 48, 162, 686, 1484; 1936, **28**, 106, 249, 489, 601, 718, 984, 1045, 1328; *Chem. Abs.*, 1934, **28**, 1254, 2253, 4297, 5744; 1935, **29**, 28, 670, 2044, 4659; 1936, **30**, 946, 1645, 3307, 3710, 4747, 6255, 6630, 7986; *Brit. Chem. Abs.* **B**, 1934, 261; **A**, 1934, 214; **B**, 1934, 707, 949; **A**, 1935, 22, 290; **B**, 1935, 886, 710; **A**, 1936, 149; **B**, 1936, 307; **A**, 1936, 675, 788, 930; *J. Inst. Pet. Tech.*, 1934, **21**, 69A, 154A, 482A, 521A, 606A; 1935, **21**, 90A, 122A, 298A; 1936, **22**, 44A, 142A, 143A, 253A, 344A, 438A, 437A.

[45] H. Staudinger and F. Staiger, *Ber.*, 1935, **68B**, 707; *Brit. Chem. Abs.* **A**, 1935, 728; *Chem. Abs.*, 1935, **29**, 4237.

[46] K. H. Meyer and A. van der Wijk, *Helv. Chim. Acta*, 1935, **18**, 1067; *Chem. Abs.*, 1935, **29**, 7738; *Brit. Chem. Abs.* **A**, 1935, 1318; *J. Inst. Pet. Tech.*, 1936, **22**, 17A.

[47] B. H. Sage, J. E. Sherborne and W. N. Lacey, *Proc. Am. Petroleum Inst. Sect. IV*, 1935, **16**, 40; *Chem. Abs.*, 1936, **30**, 3979; *J. Inst. Pet. Tech.*, 1936, **22**, 199A.

[48] Crystal oil is a water-white, refined oil, having a molecular weight between 335 and 340, with the accompanying characteristics of low volatility, narrow boiling range, and moderately high viscosity.

[49] A. A. Ashdown, L. Harris and R. T. Armstrong, *J.A.C.S.*, 1936, **58**, 850; *J. Inst. Pet. Tech.*, 1936, **22**, 298A; *Chem. Abs.*, 1936, **30**, 4823; *Brit. Chem. Abs.* **A**, 1936, 831.

[50] D. B. Pall and O. Maass, *Can. J. Research*, 1936, **14B**, 96; *Chem. Abs.*, 1936, **30**, 4063; *Brit. Chem. Abs.* **A**, 1936, 673.

[51] G. Calingaert and H. Soroos, *J.A.C.S.*, 1936, **58**, 635; *J. Inst. Pet. Tech.*, 1936, **22**, 255A; *Chem. Abs.*, 1936, **30**, 3771; *Brit. Chem. Abs.* **A**, 1936, 701.

[52] L. S. Kassel, *J.A.C.S.*, 1936, **58**, 670; *Chem. Abs.*, 1936, **30**, 4062; *J. Inst. Pet. Tech.*, 1936, **22**, 254A.

by Cox[53] (vapor pressures), Massart[54] (temperature variation of density) and Parks[55] (free-energy relations). The structure of ceresin hydrocarbons has been studied by Nametkin and Nifontova.[56] The miscibility of different types of hydrocarbons in nitromethane, diethyl sulphate, aniline and benzyl alcohol has been investigated by Mulliken and Wakeman.[57] Sage, Mendenhall and Lacey[58] have investigated the viscosity of four hydrocarbon oil solutions. The boiling points of a number of hydrocarbons[58a] of the cyclopentane and cyclohexane series are recorded in Table 6.

TABLE 6.—*Cyclopentane and Cyclohexane Hydrocarbons.*

Hydrocarbon	Formula	Boiling Point in °C.
Cyclopentane[a]	C_5H_{10}	48.5-51.0 (748 mm.)
Methylcyclopentane[b]	$C_5H_9CH_3$	71.9 (760 mm.)
1,2-Dimethylcyclopentane[c]	$C_5H_8(CH_3)_2$	94-98 (760 mm.)
1,3-Dimethylcyclopentane[d]	$C_5H_8(CH_3)_2$	90.6-90.8 (760 mm.)
cis-1-Methyl-2-ethylcyclopentane[e]	$C_5H_8(CH_3)(C_2H_5)$	127.7-128.0 (760 mm.)
trans-1-Methyl-2-ethylcyclopentane[e]	$C_5H_8(CH_3)(C_2H_5)$	121.4-121.75 (760 mm.)
1-Methyl-3-isopropylcyclopentane[f]	$C_5H_8(CH_3)(C_3H_7)$	140-142.5 (764.8 mm.)
1,2-Dimethyl-3-isopropylcyclopentane[f]	$C_5H_7(CH_3)_2(C_3H_7)$	159-160.5 (757.6 mm.)
Cyclohexane[g]	C_6H_{12}	80.3 (750 mm.)
Methylcyclohexane[g]	$C_6H_{11}(CH_3)$	100.0 (758 mm.)
cis-1,2-Dimethylcyclohexane[g]	$C_6H_{10}(CH_3)_2$	126.5 (750 mm.)
trans-1,2-Dimethylcyclohexane[g]	$C_6H_{10}(CH_3)_2$	124.5 (755 mm.)
cis-1,3-Dimethylcyclohexane[g]	$C_6H_{10}(CH_3)_2$	121.0 (760 mm.)
trans-1,3-Dimethylcyclohexane[g]	$C_6H_{10}(CH_3)_2$	119 (756 mm.)
Ethylcyclohexane[g]	$C_6H_{11}(C_2H_5)$	129.5 (756 mm.)
cis-1,3,5-Trimethylcyclohexane[g]	$C_6H_9(CH_3)_3$	140.0-140.5 (752 mm.)
trans-1,3,5-Trimethylcyclohexane[g]	$C_6H_9(CH_3)_3$	138-139 (761 mm.)
n-Propylcyclohexane[g]	$C_6H_{11}(C_3H_7)$	154.5-155.5 (756 mm.)
cis-1,2,4,5-Tetramethylcyclohexane[g]	$C_6H_8(CH_3)_4$	171 (755 mm.)
trans-1,2,4,5-Tetramethylcyclohexane[g]	$C_6H_8(CH_3)_4$	166-168 (760 mm.)
Isopropylcyclohexane[g]	$C_6H_{11}(C_3H_7)$	152-153 (756 mm.)

[a] N. D. Zelinzky, B. A. Kazanskii and A. F. Plate, *Ber.*, 1933, **66B**, 1419, *Chem. Abs.*, 1933, **27**, 5725, *Brit. Chem. Abs.* **A**, 1933, 1150.

[b] M. M. Hicks-Bruun and J. H. Bruun, *J. Research Nat. Bur. Standards*, 1931, **7**, 799; *Chem. Zentr.*, 1932, **1**, 1466; *Chem. Abs.*, 1932, **26**, 1423; *Brit. Chem. Abs* **B**, 1932, 169.

[c] M. van Rysselberge, *Bull. classe sci., Acad. roy. Belg.*, 1926, (5) **12**, 171; *Chem. Zentr.*, 1926, **4**, 1846; *Chem. Abs.*, 1927, **21**, 375; *Brit. Chem. Abs.* **A**, 1927, 47.

[d] G. Chavanne, *Bull. classe sci., Acad. roy. Belg.*, 1926, (5) **12**, 105; *Chem. Zentr.*, 1926, **4**, 1845; *Chem. Abs.*, 1926, **20**, 2664; *Brit. Chem. Abs.* **A**, 1927, 46.

[e] G. Chiurdoglu, *Bull. classe sci., Acad. roy. Belg.*, 1931, (5) **17**, 1404; *Chem. Zentr.*, 1932, **2**, 2161; *Chem. Abs.* 1932, **26**, 4311; *Brit. Chem. Abs.* **A**, 1932, 267.

[f] B. A. Kazanskii, *Ber.*, 1929, **62B**, 2209; *Chem. Abs.*, 1930, **24**, 75, *Brit. Chem Abs.* **A**, 1929, 1286.

[g] F. Eisenlohr, *Fortschr. Chem., Physik. physikal. Chem., Series B*, 1925, **18**, (9), 1; *Chem. Zentr.*, 1926, **1**, 73; *Chem. Abs.*, 1926, **20**, 171; *Brit. Chem. Abs.* **A**, 1926, 718.

THE ORIGIN OF PETROLEUM

Among the older views of the origin of petroleum, the theory of the heat decomposition of organic remains in the sedimentary rocks has long been considered possible. This so-called destructive-distillation theory was first suggested by the experiments of Warren and Storer[59] in 1863 and later by Engler[60] in 1888. Fatty oils of marine origin were believed to be the raw materials in the pyrogenesis of mineral oils. Later Seyer[61] advanced the suggestion that petroleum is formed from fatty acids of animal or vegetable origin by slow cracking at high pressures and comparatively low temperatures. One important implication of Seyer's theory is that dense saturated molecules of low hydrogen-carbon ratio, such as polycyclic naphthenes, should be produced to a greater extent with increasing time, temperature and pressure.

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[53] E. R. Cox, *Ind. Eng. Chem.*, 1936, **28**, 613; *Chem. Abs.*, 1936, **30**, 4371; *J. Inst. Pet. Tech.*, 1936, **22**, 344A; *Brit. Chem. Abs.* **A**, 1936, 788.

[54] L. Massart, *Bull. soc. chim. Belg.*, 1936, **45**, 76; *Chem. Abs.*, 1936, **30**, 4062; *Brit. Chem. Abs.* **A**, 1936, 557.

[55] G. S. Parks, *Chem. Rev.*, 1936, **18**, 325; *Chem. Abs.*, 1936, **30**, 5113. See also Chapter 54 for thermodynamic data.

[56] S. S. Nametkin and S. S. Nifontova, *J. Applied Chem. (U.S.S.R.)*, 1936, **9**, 834; *Brit. Chem. Abs.* **A**, 1936, 960; *Chem. Abs.*, 1936, **30**, 7829.

[57] S. P. Mulliken and R. L. Wakeman, *Rec. trav. chim.*, 1935, **54**, 366; *Brit. Chem. Abs.* **A**, 1935, 694; *Chem. Abs.*, 1935, **29**, 3975; *J. Inst. Pet. Tech.*, 1935, **21**, 401A.

[58] B. H. Sage, W. R. Mendenhall and W. N. Lacey, *Proc. Am. Petroleum Inst. Sect. IV*, 1935, **16**, 45; *Oil Weekly*, 1936, **80** (13), 30; *Chem. Abs.*, 1936, **30**, 3979.

[58a] A discussion of boiling-point calculations based on known boiling points of related or analogous compounds or of decomposition products is given by K. Billig, *Ber.*, 1937, **70**, 157.

However, a considerable body of data has been accumulated which would seem to support very strongly a low-temperature origin of petroleum.[62] The evidence, though circumstantial, is both chemical and geological and may be briefly summarized as follows. From the chemical viewpoint, the total absence, in petroleum and natural gas, of such typical products of thermal decomposition as hydrogen, carbon monoxide and olefin hydrocarbons, is in favor of a low temperature origin. More convincing is the existence in crude oil of certain complex sulphur, nitrogen and oxygenated organic substances readily decomposable by heat treatment, as well as of optically active constituents whose rotation would most certainly have been destroyed by prolonged exposure to even moderate temperatures.[63] Chlorophyll porphyrins, substances readily decomposable at relatively low temperatures, have also been found in many petroleums by Treibs.[64] It might be argued that some of these thermolabile substances could be formed by processes operating subsequently to the original destructive distillation, but such an explanation appears improbable. According to Brooks,[65] the presence of chlorophyll porphyrins in crude oil is an indication of (a) a low-temperature history, (b) the derivation of petroleum from, or association of the original source material with, chlorophyll-bearing plant life, probably marine algae, and (c) anaerobic conditions during the deposition of the original source material.[66]

It is a logical consequence of the destructive distillation hypothesis that, with increasing age and depth, petroleum should tend to become more and more naphthenic and heavy in character, while the younger deposits should be paraffinic. Although no entirely consistent relation has been discovered between petroleum composition and the age or depth of the deposit, the available data do not seem to be in accord with the demands of the thermal decomposition theory. From a study of the A.P.I. gravities and compositions of petroleums of different ages and depths in the Gulf Coast area, Barton[67] observed a progressive alteration of these properties with depth. Naphthenes and aromatic hydrocarbons occur to the greatest extent in the younger and shallowest Gulf Coast deposits, while the older and deeper ones are lighter and more paraffinic. This is in direct opposition to the demands of the theory. Seyer[68] emphasizes that from the chemical point of view the asphaltic and cyclic hydrocarbons must come from the paraffin hydrocarbons and not the reverse. For example, if A, B and C represent, respectively, the youthful, mature and old age stages in the life history of a petroleum, or, respectively, oils of young, middle and old geologic ages, then the base of A should be paraffinic, of B, mixed paraffinic and asphaltic, and of C, asphaltic. In support of this theory, the progressive change from naphthenic to paraffinic type with increasing age and depth does not appear to hold for certain other locations, including the fields of Wyoming[69] and California.[70] Details of the variation in properties of German petroleums at different depths of the same geological formation, as well as from different formations, have been supplied by Steinbrecher and Stutzer.[71] Pratt[72] has suggested that petroleums are progressively hydrogenated (to yield lighter and more paraffinic products) by hydrogen derived from methane, but the great stability of the methane molecule militates against the view.

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[59] C. M. Warren and F. H. Storer, *Mem. Amer. Acad. Arts and Sci.*, 1865, (2) **9**, 177; *J. Prakt. Chem.*, 1867, **102**, 436.

[60] C. Engler, *Ber.*, 1888, **21**, 1816; 1889, **22**, 592; *J.C.S.*, 1888, **54**, 928; 1889, **56**, 586.

[61] W. F. Seyer, *J. Inst. Pet. Tech.*, 1933, **19**, 773; *Brit. Chem. Abs.* B, 1933, 1042.

[62] Evidence for this has been reviewed by B. T. Brooks, *J. Inst. Pet. Tech.*, 1934, **20**, 177; *Chem. Abs.*, 1934, **28**, 3694; *J. Inst. Pet. Tech.*, 1934, **20**, 276A.

[63] B. T. Brooks, *loc. cit.* See also M. Rakusin (*J. Russ. Chem. Soc.*, 1906, **38**, 790; *Chem. Zentr.*, 1907, **1**, 841) for early treatment of optical phenomena in connection with petroleum

[64] A. Treibs, *Ann.*, 1934, **510**, 42; *Brit. Chem. Abs.* A, 1934, 629; *Chem. Abs.*, 1934, **28**, 7211.

[65] B. T. Brooks, *Bull. Am. Assoc. Petroleum Geol.*, 1936, **20**, 280; *Chem. Abs.*, 1936, **30**, 4124; *J. Inst. Pet. Tech.*, 1936, **22**, 178A.

[66] See also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[67] D. C. Barton, *J. Inst. Pet. Tech.*, 1934, **20**, 206; *Chem. Abs.*, 1934, **28**, 4577; *Brit. Chem. Abs.* A, 1934, 507; *J. Inst. Pet. Tech.*, 1934, **20**, 276A. *Bull. Amer. Assoc. Petroleum Geol.*, 1934, **18**, 143; *Chem. Abs.*, 1934, **28**, 1632.

[68] W. F. Seyer, *Bull. Amer. Assoc. Petroleum Geol.*, 1933, **17**, 1251; *J. Inst. Pet. Tech.*, 1933, **19**, 773; *Chem. Abs.*, 1934, **28**, 300; *Brit. Chem. Abs.*, B, 1933, 1042.

Courtesy Standard Oil Co. of California

FIG. 1A.—Pressure Stills.

It has been shown that the available chemical evidence, when considered as a whole, favors a low temperature history for petroleum which, however, is even more strongly supported by the geological data. Thus, Illing[73] states that the geological evidence demands a theory of petroleum origin almost contemporaneous with the sediments, and not, as the distillation theory indicates, as a later process of metamorphism. Views up to 1931 regarding source beds for petroleum have been discussed by Snider[74] and also by Trask and Hammar.[75] The temperatures observed in oil-bearing strata are all relatively low, bottom hole temperatures in some of the most prolific fields yielding oil from geologically younger sands being not in excess of 100°F. The rise in temperature with increasing depth is very gradual (being 1°F. per 52 ft. in Fullerton, California, and 1°F. per 70 ft. in Ozona, Texas). Temperatures noted at depths around 7000 ft. varied from 150°F. to 170°F.[76] Moreover, the geological evidence is in harmony with the view that the present observed temperatures must be near the maximum over the geological epoch during which petroleum could have been formed. This position has been summed up by McCoy and Keyte[77] with the statement that most of the known oilfields were undoubtedly formed at temperatures below 140°F. McCoy concludes that from evidence in another of his papers,[78] it is not very probable that oil accumulation has necessitated 60 million or more years to have been accomplished.

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[69] J. G. Bartram, *Bull. Amer. Assoc. Petroleum Geol.*, 1934, **18**, 157.

[70] J. A. Taff, *Bull. Amer. Assoc. Petroleum Geol.*, 1934, **18**, 177.

[71] H. Steinbrecher and O. Stutzer, *Petroleum Z.*, 1934, **30** (39), 1; *Brit. Chem. Abs.* **B**, 1934, 995; *J. Inst. Pet. Tech.*, 1934, **20**, 566A.

[72] W. E. Pratt, *Bull. Amer. Assoc. Petroleum Geol.*, 1934, **18**, 235.

The chemical and geological evidence is in agreement with the view that petroleum is the result of low temperature anaerobic fermentation of organic matter, deposited in sediments as solid or semi-solid material. Unfortunately, very few attempts have been made to obtain experimental evidence as to the rôle of bacteria in petroleum formation, especially under alkaline anaerobic conditions. Taylor's[79] work concerned the slow anaerobic degradation of fatty oils and acids under sodium clay.[80] He found that triacetin under these conditions yielded methane alone, while gaseous paraffins were produced from tributyrin. Stearic and palmitic acids were slowly attacked, but the products were not examined. At present the depths in the sediments at which bacterial action ceases is in dispute, but the vertical distribution of bacteria in marine sediments has been investigated by ZoBell and Anderson.[81]

The principal types of organic substances which need to be considered as possible main source materials for petroleum formation in sedimentary rocks are cellulose, proteins, lignins, oleo-resins, waxes and fatty oils.[82] Of these, lignins, oleo-resins and waxes are resistant to bacterial action. Proteins, fatty oils and cellulose are decomposable by anaerobic bacteria, the latter type furnishing methane almost exclusively. Brooks,[83] from a detailed survey of the available evidence, concluded that the fatty oils are still to be regarded as the most likely source materials for petroleum formation.

The identification and isolation of desoxo-phyllerythrin (formula I) and desoxophyllerythro-ätioporphyrin (formula II) in an oil shale found in the alpine

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[73] V. C. Illing, Discussion in *J. Inst. Pet. Tech.*, 1926, **12**, 281.

[74] L. C. Snider, in "Problems of Petroleum Geology," edited by W. E. Wrether and F. H. Lahee, American Association of Petroleum Geologists, Tulsa, Oklahoma, **1934**, 51.

[75] P. D. Trask and H. E. Hammar, "Origin and Environment of Source Sediments of Petroleum," Gulf Publishing Co., Houston, Texas, **1932**.

[76] C. E. Van Orstrand, *Oil & Gas J.*, 1928, **26** (48), 39.

[77] A. W. McCoy and W. R. Keyte, in "Problems of Petroleum Geology," *loc. cit*, 253.

[78] A. W. McCoy, in "Problems of Petroleum Geology," *loc. cit.*, 581

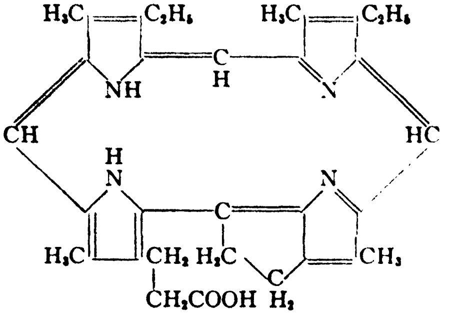
[79] E. McK. Taylor, *J. Inst. Pet. Tech.*, 1928, **14**, 825; *Brit. Chem. Abs* **A**, 1929, 168; *Chem Abs.*, 1929, **23**, 2024.

[80] Sodium clay is a characteristic constituent of sediments formed under marine, estuarine or deltaic conditions.

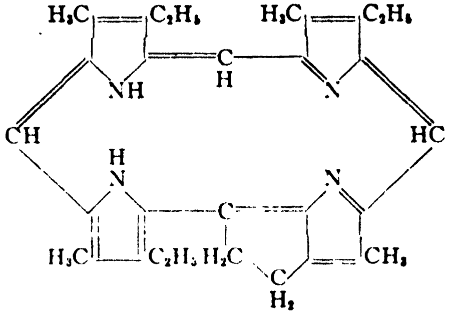
[81] C. E. ZoBell and D. Q. Anderson, *Bull. Amer. Assoc. Petroleum Geol.*, 1936, **20**, 258; *J. Inst Pet. Tech.*, 1936, **22**, 179A; *Chem. Abs.*, 1936, **30**, 4528.

[82] B. T. Brooks, *J. Inst. Pet. Tech.*, 1934, **20**, 177; *Chem. Abs.*, 1934, **28**, 3694; *J. Inst. Pet Tech.*, 1934, **20**, 276A.

[83] B. T. Brooks, *loc. cit.*

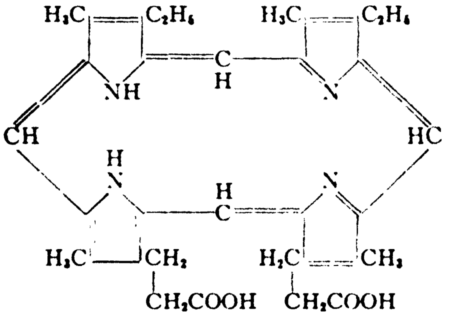


I.

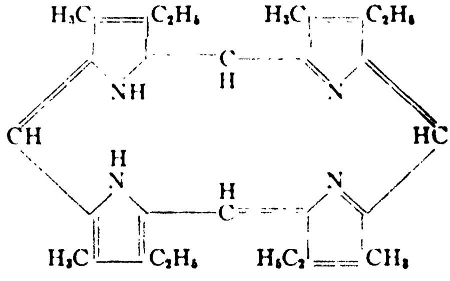


II.

triassic[84] and the further identification[85] in this isolated portion of mesoporphyrin (formula III) and meso-ätioporphyrin (formula IV) led Treibs[86] to the conclusion that petroleum probably had its genesis from chlorophyll containing material such as the shallow-water plankton.



III.



IV.

Fish remains are considered by Henderson[87] to be insufficient in amount to account for the large quantities of petroleum occurring in some formations. The development of oil through a fossil-resin stage from the same source materials as those yielding coal has been suggested by Briggs.[88] Fester and Cruellas[89] assume that petroleum is derived from the fatty material remaining after the bacterial decomposition of marine flora and fauna in tropical climates; whereas, in colder climates, cellulose and lignin did not undergo complete decomposition and varieties of coal were the ultimate results. Colloidal vanadium sulphides, which are present in South American petroleums, probably exert a catalytic action on the processes of organic change, according to Fester and Cruellas.[90]

If anaerobic decay of organic material in sediments is the origin of petroleum, it might be expected that protopetroleums in transition stages will be found in geologically recent strata in the form of solid or semi-solid material. Brooks[91] suggests that such material will possibly consist of a mixture of hydrocarbon oils together with polymerized fatty or naphthenic acids.

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[84] A. Treibs, *Ann.*, 1934, **509**, 103; *Chem. Abs.*, 1934, **28**, 3694; *Brit. Chem. Abs.* **A**, 1934, 387.

[85] A. Treibs, *Ann.*, 1934, **510**, 42; *Chem. Abs.*, 1934, **28**, 7211; *Brit. Chem. Abs.* **A**, 1934, 629.

[86] A. Treibs, *loc. cit.*

[87] J. Henderson, *Science*, 1935, **81**, 176; *Brit. Chem. Abs.* **A**, 1935, 600.

[88] H. Briggs, *Proc. Roy. Soc. Edinburgh*, 1934, **54**, 115; *Brit. Chem. Abs.* **B**, 1934, 994.

[89] G. A. Fester and J. Cruellas, *Rev. facultad quim. ind. agr., Univ. nacl. litoral*, 1934, **3**, 76; *Brit. Chem. Abs.* **A**, 1936, 51; *Chem. Abs.*, 1935, **29**, 6179.

[90] G. A. Fester and J. Cruellas, *loc. cit.*

[91] B. T. Brooks, *J. Inst. Pet. Tech.*, 1934, **20**, 177; *J. Inst. Pet. Tech.*, 1934, **20**, 276A; *Chem. Abs.*, 1934, **28**, 3694.

Synthetic oils similar to petroleum have been prepared by Berl and Biebesheimer[92] by the hydrogenation of the product obtained by digesting cellulosic material with aqueous alkalies at 310-330°C. and 180-200 atmospheres pressure. They proposed the theory that petroleum had its origin under similar conditions and that asphalt was formed if reaction took place at shallow depths where oxidation could occur.

Careful fractionation of Hodonin (Czechoslovakia) crude oils at absolutely constant pressure has been found by Wenzel and Weiser[93] to yield maximum cuts corresponding to hydrocarbons having 15 and 20 carbon atoms per molecule in one case, and to those having 13, 15, 20, 25 and 28 carbon atoms in a second instance. A terpenic origin is suggested to explain this observation. Oxidation of one fraction, having the empirical composition of $C_{28}H_{46}$, with potassium permanganate in hot acetone furnished phthalic acid, from which it was concluded that the parent-hydrocarbon had the constitution o-$C_6H_4(CH_2C_{10}H_{19})_2$, the $C_{10}H_{19}$ radicals being naphthenic residues. Wenzel and Weiser suggest that such a compound could be formed from squalene by condensation of the latter accompanied by aromatization and loss of two methyl groups. The results are interpreted as indicating the derivation of petroleum from marine plants.

NATURAL GAS

The production and utilization of natural petroleum gases is being carried out in many parts of the world, notably in Russia, Persia, Poland, Rumania, Germany, Italy and British India, but the industry has attained its greatest importance in the United States, of which Texas is the largest producer. The quantities produced in the United States in 1933 and 1934 were 1555 billion cu. ft. and 1770 billion cu. ft., respectively.[94] The present known natural gas reserves of the United States are reported sufficient to last for many years at the present rate of consumption. Thus, it is estimated that the Amarillo field of Texas will continue to supply gas at the present rate for at least 60 years. Of interest in this connection is the discovery of large reservoirs of natural gas in the deeper strata in northern Pennsylvania and New York, where pressures as high as 2250 pounds per sq. in. are encountered at depths of 4000-5000 ft.[95] In 1933 half of the natural gas produced in the United States was used as an industrial and domestic fuel and the remainder in the oil fields and for carbon black manufacture. In fact, the amount of natural gas consumed annually (at the 1933 rate) is equal in heating value to about 70 million tons of bituminous coal.

Natural petroleum gases consist essentially of a mixture of lower paraffin hydrocarbons as well as varying proportions of nitrogen, carbon dioxide and traces of rare gases such as helium. Hydrogen and carbon monoxide are uniformly absent. In the so-called dry gases, methane is the main hydrocarbon constituent, and the wet gases usually contain, in addition, appreciable proportions of the higher paraffins (ethane, propane, *n*-butane, isobutane, *n*-pentane, isopentane or neopentane). The wet gases are usually treated for the recovery of volatile liquid constituents—the so-called natural gasoline.[96]

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[92] E. Berl and H. Biebesheimer, *Ann.*, 1933, 504, 38; *Chem. Abs.*, 1934, **28**, 3693. E. Berl, *Science*, 1934, **80**, 227; *Chem. Abs.*, 1934, **28**, 6660; *Brit. Chem. Abs.* **A**, 1934, 1198.

[93] F. Wenzel and H. Weiser, *J. prakt. Chem.*, 1936 (2), **144**, 145; *Brit. Chem. Abs.* **B**, 1936, 226.

[94] G. R. Hopkins and H. Backus, "Natural Gas in 1934," U. S. Bureau of Mines; *J. Inst. Pet. Tech.*, 1936, **22**, 176A.

[95] G. A. Burrell, *Ind. Eng. Chem.*, 1934, **26**, 143; *Chem. Abs.*, 1934, **28**, 1840; *Brit. Chem. Abs.* **B**, 1934, 227.

[96] For a general discussion and classification of natural gases, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

Isolation and identification of the various hydrocarbon constituents of natural gases are readily accomplished by low-temperature fractional distillation, a process which is now standardized as an analytical procedure. By this method, ethane, propane, *n*-butane and isobutane have been secured in pure condition from liquefied Polish natural gas by Kling and Wiecławek.[97] Wet gas from a well near Pittsburgh was found to contain benzene to the extent of nearly 18 parts per million.[98] The carbon dioxide content of natural gases is variable although in special cases it may be present as the preponderant constituent. Thus, wells delivering a gas containing 98.6 per cent of carbon dioxide with a remainder of nitrogen and helium and no hydrocarbons or hydrogen sulphide have been found in New Mexico and serve as a ready source of this dioxide.[99] According to Wittich,[100] such incombustible gases are being utilized in Mexico for power production by virtue of their high pressure, as well as in the manufacture of solid carbon dioxide. Gases of analogous characteristics have been obtained from wells in Colorado,[101] the composition of one being: methane, 0.52 per cent; ethane, 3.95 per cent; carbon dioxide, 92.14 per cent; oxygen, 0.09 per cent; nitrogen, 3.16 per cent; and helium, 0.14 per cent.[102] Large proportions of this dioxide and only small amounts of methane are present in the gases from borings in the Tuscan boraciferous regions of Italy.[103]

Although usually present only in traces, nevertheless helium does occur to the extent of 1.8 per cent in a natural gas from the Cliffside structure near Amarillo, Texas. Separation is effected by a process of fractional liquefaction (after removal of carbon dioxide) at a net cost of about 8.6 dollars per 1000 cu. ft. of helium produced.[104] The argon-nitrogen ratio in natural gases has been found by Geslin[105] to be less than for air, a fact which is attributed to dilution with nitrogen derived from the decomposition of animal and vegetable material. A method of determining helium and argon in natural gases has been described by Gerling.[106] Snow and Johnston[107] report that a sample of butane from an Oklahoma field contained 30 per cent more deuterium than corresponds with the content of this element present in ordinary hydrogen.

The compositions of a large number of natural gases (from different fields) have been determined,[108] including those from Germany,[109] particularly the Merihagen field,[110] Poland,[111] Austria,[112] France,[113] British India, Burma and Assam[114] and Russia,[115] especially those from the Grozny,[116] Apsheron[117] and Baikal Lake[118] districts.

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[97] K. Kling and B. Wieclawek, *Przemysl Chem.*, 1934, **18**, 424; *Chem. Abs.*, 1935, **29**, 6021; *Brit Chem. Abs.* **B**, 1935, 132; *J. Inst. Pet. Tech.*, 1935, **21**, 46A.

[98] H. H. Schrenk, W. P. Yant and S. J. Pearce, Bur. Mines Rept. of Investigations No 3293, 1935; *Chem. Abs.*, 1936, **30**, 269.

[99] E. R. Harrington, *Refrigerating Eng.*, 1935, **29**, 137; *Chem. Abs.*, 1935, **29**, 3787.

[100] E. Wittich, *Gas u. Wasserfach*, 1934, **77**, 417; *Brit. Chem. Abs.* **B**, 1934, 788; *Chem. Abs.*, 1934, **28**, 5962.

[101] J. C. Miller, *U. S. Geol. Surv. Circ.*, **1934**, No. 5; *J. Inst. Pet. Tech.*, 1934, **20**, 269A.

[102] L. G. E. Bignell, *Oil & Gas J.*, 1935, **34** (29), 13; *J. Inst. Pet. Tech.*, 1936, **22**, 78A.

[103] G. Conti, *Giorn. Chim. Ind. Appl.*, 1933, **15**, 500; *Brit. Chem. Abs.* **B**, 1934, 93.

[104] H. S. Kennedy and C. W. Seibel, Minerals Yearbook, **1935**, 867. See also Carleton Ellis, *loc. cit.*, page 12.

[105] M. Geslin, *Compt. rend.*, 1935, **200**, 1137; *Brit. Chem. Abs.* **A**, 1935, 724; *Chem. Abs.*, 1935, **29**, 4298.

[106] E. K. Gerling, *J. Applied Chem. (U.S.S.R.)*, 1933, **6**, 1153; *Chem. Abs.*, 1934, **28**, 3872.

[107] R. D. Snow and H. L. Johnston, *Science*, 1934, **80**, 210; *Brit. Chem. Abs.* **A**, 1934, 1198; *Chem. Abs.*, 1934, **28**, 7152.

[108] S. Hummel, *Petroleum Z.*, 1935, **31** (6), 13; **31** (9), 21; **31** (14), 1; **31** (18), 9; **31** (22), 9; **31** (27), 9; **31** (35), 17; *Chem. Abs.*, 1935, **29**, 8299.

[109] H. Stille and H. Schlüter, *Bull. Am. Assoc. Petroleum Geol.*, 1934, **18**, 719; *Chem. Abs.*, 1934, **28**, 6980.

[110] See, *Chem.-Ztg.*, 1935, **59**, 136; *J. Inst. Pet. Tech.*, 1935, **21**, 117A, 203A.

[111] K. Tolwinski, *Bull. Amer. Assoc. Petroleum Geol.*, 1934, **18**, 892; *Chem. Abs.*, 1934, **28**, 6980.

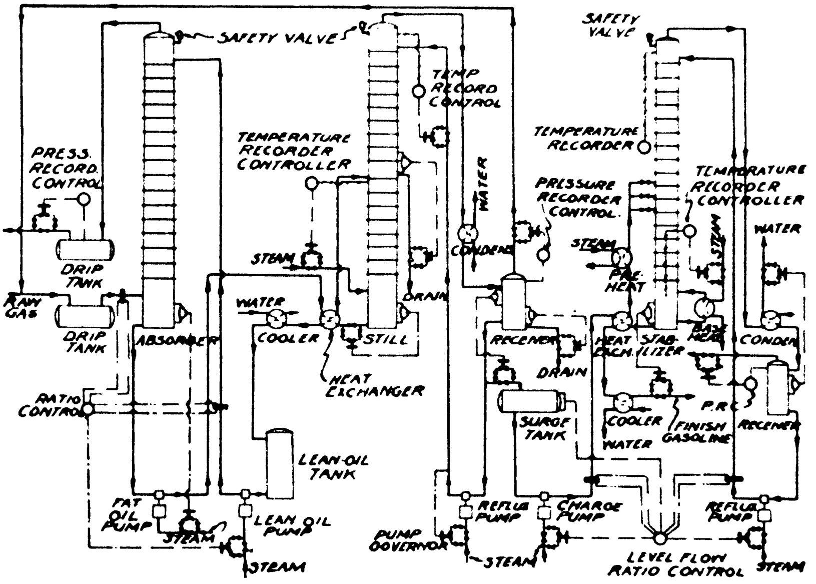
[112] L. Teissl, *Ztschr. Oest. Ing. Arch.*, 1935, **V**, 46; *J. Inst. Pet. Tech.*, 1935, **21**; 203A.

[113] V. Charrin, *J. usines gaz*, 1936, **60**, 49; *Chem. Abs.*, 1936, **30**, 5394.

[114] G. P. Kane, K. R. Krishnaswami and H. E. Watson, *J. Indian Inst. Sci.*, 1934, **17A**, 33; *Brit Chem. Abs.* **B**, 1934, 612; *Chem. Abs.*, 1934, **28**, 4569. C. T. Barber, *Mem. Geol. Survey India*, 1935, **66**, Pt. 1, 172; *Chem. Abs.*, 1935, **29**, 6397.

UTILIZATION

As already mentioned, the most important applications of natural gas are as a fuel for both domestic and industrial purposes and as raw material for the manufacture of carbon black.[119] Among other uses for which natural gas has been suggested are the preparation of halogen derivatives of methane, ethane, propane and pentane, monohydric alcohols, acetone, acetic acid and formaldehyde.[119a] In addition, the wet gases are usually treated for the recovery of natural gasoline and also of the so-called liquefied gases, propane and butane. Before these liquid and readily liquefiable constituents are separated, the gas is freed from hydrogen sulphide, usually by passage through a bed of iron oxide or by absorption in a solution of a suitable weak base.[120] Removal of liquid hydrocarbons can be effected either by compression, charcoal adsorption or by oil absorption, but the latter system is now generally employed. The charcoal adsorption process has,



Courtesy Industrial and Engineering Chemistry

FIG. 2—Flow Diagram of Stabilizing Unit of Natural Gasoline Plant. (G. A. Burrell)

since the advent of the stabilizer, lost the advantages it originally possessed over the rival methods of furnishing a gasoline of relatively low vapor pressure. Moreover, it also suffers from the disadvantages that charcoal is expensive, heat exchange is difficult and minute oil sprays cause a deterioration in charcoal activity. For these reasons oil absorption, in which the gas is washed with oil under pressure in bubble type absorbers, is favored in modern practice. The more volatile constituents, propane and butanes, of the resulting gasoline are removed in pressure fractionating columns, or stabilizers of the bubble type, and constitute the so-called liquefied petroleum gases. The developments and improvements for the 20 years prior to 1934 in the design of absorption plants have been described by Burrell[121] and by Kallam.[122] (See Fig. 2.) An account of the principles of design and operation of such plants has been supplied by Burrell and Turner.[123]

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[115] C. Bohdanowicz, *Bull. Amer. Assoc. Petroleum Geol.*, 1934, **18**, 746; *Chem. Abs.*, 1934, **28**, 5209; *J. Inst. Pet. Tech.*, 1934, **20**, 436A.

[116] A. N. Sakhanov, A. I. Doladugin and I. I. Lapkin, *Gosudarstvennoe Nauch.-Tekh. Izdatelstvo Moscow-Petrograd*, **1931**, 3; *Chem. Abs.*, 1934, **28**, 295.

[117] L. Potolovskii and A. Atal'yan, *Azer. Neft. Khoz.*, **1933**, No. 5, 38; *Chem. Abs.*, 1934, **28**, 6980.

[118] V. V. Golubev and R. I. Ginzburg, *O.N.T.I. Gorno-Geol.-Neftyanoe Izdat., Crude Oils, Bitumens and Gases from Non-Caucasian Deposits*, **1934**, 259; *Chem. Abs.*, 1935, **29**, 1967.

[119] See Chapters 7 and 8.

[119a] I. N. Beall, *Refiner*, 1936, **15**, 407; *J. Inst. Pet. Tech.*, 1937, **23**, 17A.

[120] Several methods for the elimination of hydrogen sulphide from gases are discussed in Chapter 19.

Propane and butane, now being used extensively in liquid form as fuel, are by-products of the stabilization of natural gasoline. The actual proportion of these hydrocarbons in the wild gasoline[124] depends primarily on the quantity of absorption oil employed per unit volume of gas washed.

The stabilizer is usually operated so as to eliminate all the propane and most of the butane from the wild gasoline. Pressure fractionating equipment is now available, capable of separating efficiently and recovering in pure form all hydrocarbons up to and including the pentanes in natural gas and natural gasoline.[125] In the usual mode of operation the raw distillate from the stabilizer passes through a preheater and heat exchanger to a butane column from which butane is extracted at the base, a mixture of propane and ethane constituting the overhead product. The latter passes to a high pressure column from which pure propane is withdrawn at the bottom and ethane as the overhead product. Working pressures are usually about 300-400 pounds per sq. in. on the butane column and from 400 to as high as 600 pounds per sq. in. on the propane column, depending upon the operating temperatures.

The importance of liquefied propane and butane is increasing rapidly, particularly as domestic and industrial fuels.[126] The production of these materials has increased from 222,000 gallons in 1922 to 48,173,000 gallons in 1934.[127] These figures do not include large quantities of these gases which are used at the place of production as raw material in the manufacture of solvents, or as refrigerants and fuels. Gases for industrial purposes are distributed principally in special tank cars, but with the development of high tensile strength sheets there has been an increasing use of trucks and trailers. "Bottled gas," distributed in many parts of the

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[121] G. A. Burrell, *Ind. Eng. Chem.*, 1934, **26**, 143; *Chem. Abs.*, 1934, **28**, 1840; *Brit. Chem. Abs.* **B**, 1934, 227.

[122] F. L. Kallam, *Chem. Met. Eng.*, 1934, **41**, 355; *Chem. Abs.*, 1934, **28**, 6290; *Brit. Chem. Abs.* **B**, 1934, 788; *J. Inst. Pet. Tech.*, 1934, **20**, 573A. *Petroleum Engr.*, 1934, **5** (9), 17; *Chem. Abs.*, 1934, **28**, 6557; *J. Inst. Pet. Tech.*, 1934, **20**, 495A.

[123] G. A. Burrell and N. C. Turner, *Nat. Pet. News*, 1934, **26** (10), 26; **26** (11), 22; *Chem. Abs.*, 1934, **28**, 4580; *J. Inst. Pet. Tech.*, 1934, **20**, 417A.

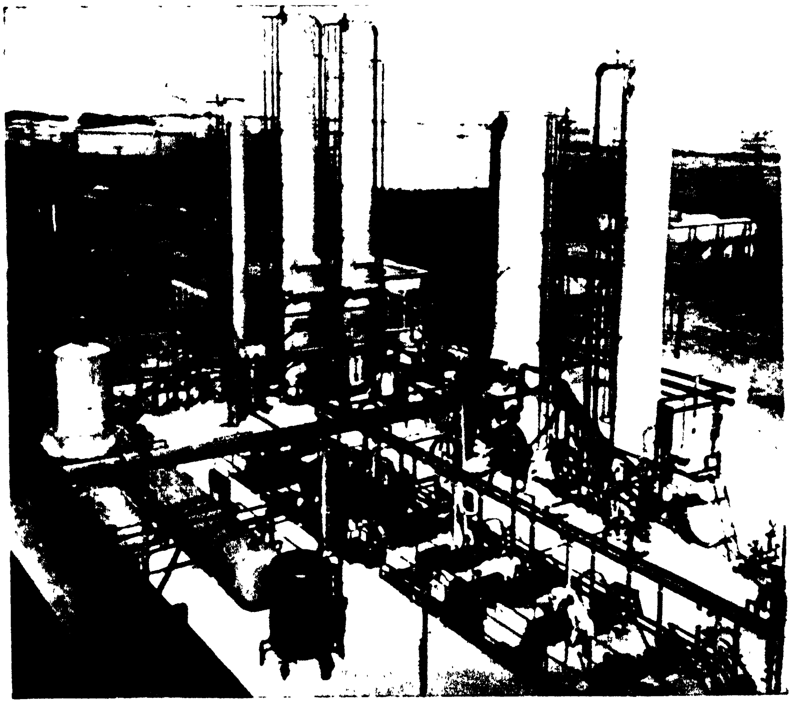
[124] Wild gasoline is a very low-boiling fraction of gasoline.

[125] The principles and operation of stabilizers are described by I. N. Beall (*Refiner*, 1934, **13**, 184, 277, 346; *Chem. Abs.*, 1934, **28**, 6290, 6990), J. C. Albright (*Refiner*, 1934, **13**, 285; *Chem. Abs.*, 1934, **28**, 6290) and N. Mayer (*Chem.-Ztg.*, 1934, **58**, 357; *J. Inst. Pet. Tech.*, 1934, **20**, 418A; *Brit. Chem. Abs.* **B**, 1934, 530). For a survey of the sources and separation of condensed propane and butane, both from crude petroleum and the cracking process, see J. Brand, *Gas u. Wasserfach*, 1934, **77**, 861; *Brit. Chem. Abs.* **B**, 1935, 132; *Chem. Abs.*, 1935, **29**, 1972.

[126] M. J. Conway, *Oil & Gas J.*, 1936, **35** (5), 57; *J. Inst. Pet. Tech.*, 1936, **22**, 350A. The compressibility of butane-air mixtures below one atmosphere pressure is of importance in the industrial application of liquid butane as a fuel, and such measurements have been made by F. W. Jessen and J. H. Lightfoot, *Ind. Eng. Chem.*, 1936, **28**, 870; *Chem. Abs.*, 1936, **30**, 5848; *J. Inst. Pet. Tech.*, 1936, **22**, 437A.

[127] W. H. Bateman, *Refiner*, 1936, **15**, 135; *J. Inst. Pet. Tech.*, 1936, **22**, 295A. A statistical review of the progress of the liquefied petroleum gas industry is given by G. G. Oberfell (*Gas Age-Record*, 1934, **73**, 179; *Chem. Abs.*, 1934, **28**, 4577).

United States is mainly propane (or propane and propene). In some instances, small quantities of butane may be present when its lower volatility does not necessitate the application of heat. Tentative specifications for some of these liquefied gas mixtures include the following.[128] Commercial propane shall consist of at least 95 per cent of propane plus propene and the residue (as determined by the mercury freezing test) shall not exceed 2 per cent by volume. Corrosive sulphur compounds shall be absent and the concentration of relatively inactive organic sulphur shall not exceed 15 g. per 100 cu. ft. of vapor. In the case of commercial butanes, the predominant hydrocarbons present should be butanes and butenes. The vapor pressure at 105°F. must not exceed 75 lbs. per sq. in. gage. Not less than 95 per cent of the material shall evaporate below 34°F. in the open cylinder weather test. Sulphur limitations are the same as for commercial propane, and freedom from entrained water is also necessary in each case. The product known as industrial propane usually consists of at least 70 per cent by liquid volume of propane (and propene). Industrial butanes containing 50 per cent of butane are also marketed.



Courtesy Foster Wheeler Corp.

FIG. 3.—Vapor Absorption and Stabilization Plant. High- and low-pressure absorbers equipped with internal coolers and gas-ratio controllers.

The largest use of bottled propane has been in kitchen ranges and water heaters, while butane has been predominant in the industrial field. However, propane has the advantages of low boiling point, high octane number, refrigeration qualities and value as a metal-cutting fuel.[129] The application of these gases in industrial furnace heating, particularly in the steel industry, has been described by Jamison and Bateman.[130] Some of the advantages are improved control both of temperature and atmosphere, reduced maintenance on furnace refractory and alloy parts and reduced scaling of product. The significance of propane and butane in the gas industry has been outlined by Brückner[131] who states that their low ignition velocities preclude their employment in welding. Cold enrichment of water-gas also is a possible application of such gases.

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[128] W. H. Bateman, *loc. cit.* T. W. Legatski and W. Z. Friend, Meeting of Amer. Chem. Soc., Petroleum Division, San Francisco, Aug., 1935.

Both propane and butane possess certain advantages as a fuel in internal combustion engines, including high octane numbers, decreased oil consumption and carbon formation and high volatility, the latter property insuring uniform distribution in the cylinders. Yet, the general replacement of gasoline by liquefied gases as an automotive fuel as yet does not appear wholly feasible, since storing and distributing costs are high and special pressure fittings are necessary. However, possible applications are in large high-powered stationary engines or in rail cars and trains where high power output is demanded and high compression ratios are permissible.[132] According to Albright,[133] a fuel consisting of 80 per cent butane and 20 per cent propane and having an octane number of 100 is being used on heavy duty commercial units. The fuel is reduced to atmospheric pressure through two regulators, and carburetion is effected in the original carburetors or in specially designed mixing chambers. The question of the use of butane as an automotive fuel has been also discussed by Barnard.[134] He concludes that this material cannot be economically adapted for small units but is suitable for railway service. In fact, this hydrocarbon was first used successfully as fuel in 1930 by the Los Angeles Railway Company with advantages which included better lubrication, less carbon deposition and diminished valve pitting and burning.[135] The development of butane as a rail car fuel has been analyzed by Stockman.[136] Fuel consumption per mile is higher with butane than with gasoline, but this is said to be more than balanced by the increase in power and speed.[137] The possibility of using propane and butane in combustion motors has received particular attention in Germany, where a liquefied gas containing 60 per cent of the propane and 40 per cent of butane (called Deurag) is marketed for this purpose.[138] One important application of these gaseous fuels is in airships. Thus, mixtures of hydrogen and propane or hydrogen and butane having the same density as air are proposed by de

[129] See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**, 16.

[130] E. A. Jamison and W. H. Bateman, *Iron Steel Engr.*, 1934, 11, 344; 1935, **12**, 209; *Chem Abs.*, 1934, **28**, 6973; 1935, **29**, 3805. *Cf.* J. K. Koeneman, *Gas*, 1936, **12** (10), 61; *Chem. Abs.*, 1936, **30**, 8571.

[131] H. Brückner, *Gas u. Wasserfach*, 1934, 77, 425; *Chem. Abs.*, 1934, **28**, 5962; *Brit. Chem. Abs.* **B**, 1934, 707.

[132] W. Z. Friend and F. Q. Beckwith, *S. A. E. Journal*, 1935, **36**, 36; *J. Inst. Pet. Tech.*, 1935, **21**, 142A; *Chem. Abs.*, 1935, **29**, 2334. L. R. Smith, *Oil & Gas J.*, 1936, **35** (21), 45; *J. Inst. Pet. Tech.*, 1936, **22**, 532A. W. T. Ziegenhain *Oil & Gas J.*, 1936, **35** (18), 51; *Chem. Abs.*, 1936, **30**, 8571. M. M. Holm, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 299; *J. Inst. Pet. Tech.*, 1936, **22**, 506A; *Chem. Abs.*, 1936, **30**, 5755.

[133] J. C. Albright, *Nat. Pet. News*, 1935, **27** (9), 48; *J. Inst. Pet. Tech.*, 1935, **21**, 179. See also Chapter 44.

[134] D. P. Barnard, *S. A. E. Journal*, 1934, **35**, 399; *J. Inst. Pet. Tech.*, 1935, **21**, 30A; *Chem. Abs.*, 1935, **29**, 908.

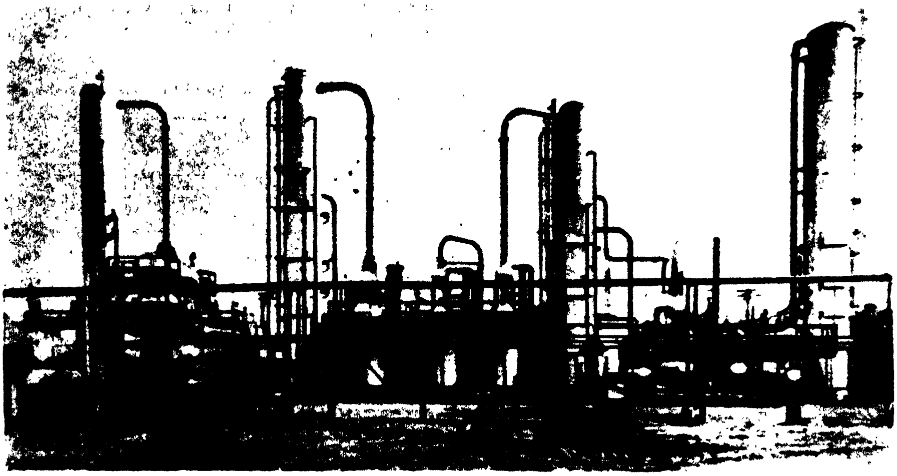
[135] L. V. Newton, *S. A. E. Journal*, 1934, **35**, 402. The use of butane as a bus fuel has also been described by H. Sherman (*Mass Transportation*, 1935, **31**, 71; *Chem. Abs.*, 1935, **29**, 3805).

[136] L. P. Stockman, *Oil & Gas J.*, 1934, **33** (3), 36; *J. Inst. Pet. Tech.*, 1934, **20**, 467A.

[137] Similar results were obtained by C. J. Vogt (*Oil & Gas J.*, 1935, **34** (26), 52; *Refiner*, 1935, **14**, 542; *J. Inst. Pet. Tech.*, 1936, **22**, 29A; *Chem. Abs.*, 1936, **30**, 2726).

[138] See, *Chem. Fabr.*, **1935**, 220; *J. Inst. Pet. Tech.*, 1935, **21**, 316A. The use of propane and butane as motor fuels has also been reveiwed by C. J. Vogt (*Automotive Ind.*, 1934, **71**, 348; *Chem. Abs.*, 1935, **29**, 317) and E. H. B. Ludwig (*Z. Osterr. Ver. Gas- Wasserfach*, 1934, **74**, 121, 132; *Chem. Abs.*, 1935, **29**, 1230).

Florez[139] for the purpose. It is pointed out by Alden[140] that an increase in the butane content of gasoline would effect several economies, but such increase is limited by the question of vapor lock which may require redesigning of the engines. Other possible industrial applications of liquefied butane and propane are in the cutting of steel (in place of acetylene), the brazing of metals and alloys, the welding of aluminum and lead burning,[141] as well as in refrigeration. Other hydrocarbon gases, including methane[142] and coal gas,[143] have been considered as motor fuels. Such gases, as well as those previously discussed, need to be stored under high pressures in cylinders, which introduces the grave drawback of much extra weight.[144]



Courtesy Foster Wheeler Corp.

FIG. 4—Debutanizing Plant. Daily capacity 15,000 barrels of raw pressure distillate.

It has been shown by Hammerschmidt[145] that the lower paraffin hydrocarbons are capable of forming relatively high-melting solid hydrates with water vapor. The melting point of the mixed hydrates from a natural gas (in a transmission line) varied with the pressure from 34°F. at 110 pounds per sq. in. to about 60°F. at 800 pounds. This shows the importance of adequate drying of hydrocarbon gases in facilitating the handling and transport of such substances under pressure.

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[139] L. de Florez, U. S. P. 1,936,155 and 1,936,156, Nov. 21, 1933, to Texas Co.; *Brit. Chem. Abs.* B, 1934, 708, *Chem. Abs.*, 1934, **28**, 882.

[140] R. C. Alden, *Refiner*, 1934, **13** (6), 208; *Chem. Abs.*, 1934, **28**, 5647

[141] M. J. Conway, *Oil & Gas J.*, 1936, **35** (5), 57; *J. Inst. Pet Tech* 1936, **22**, 350A. *Cf.* H Bruckner, *Gas u Wasserfach*, 1934, 77, 425; *Chem. Abs.*, 1934, **28**, 5962; *Brit. Chem. Abs.* B, 1934, 707.

[142] C. Padovani, *Proc. World Petroleum Congr.*, 1933, **2**, 795; *Chem. Abs.*, 1934, **28**, 3866; *Brit Chem. Abs* B, 1934, 996

[143] R. Cook, *Gas J.*, 1936, **213**, 90; *Chem. Abs.*, 1936, **30**, 1973. F. B. Halliwell, *Gas J.*, 1934, **206**, 39; *J. Inst. Pet. Tech.*, 1934, **20**, 340A; *Chem. Abs.*, 1934, **28**, 3559. C. M. Walter, *Proc. World Petroleum Congr.*, 1933, **2**, 764; *Chem. Abs.*, 1934, **28**, 3865; *Brit. Chem. Abs.* B, 1934, 743. R. Cook, *J. Inst. Fuel*, 1935, **9**, 125; *Chem. Abs.*, 1936, **30**, 4649; *Brit. Chem. Abs.* B, 1936, 226.

[144] The use of gaseous motor fuels in Germany is described by M. H. Kraemer (*Z. Ver. deut. Ing.*, 1934, **78**, 1235; *J. Inst. Pet. Tech.*, 1935, **21**, 102A), W. G. Rumbold (*Gas World*, 1933 **99** (2576), 121; *Chem. Abs*, 1934, **28**, 875; *J. Inst. Pet. Tech.*, 1934, **20**, 119A) and by W. Benninghoff (*Z. Ver. deut. Ing.*, 1935, **79**, 203; *J. Inst. Pet. Tech.*, 1935, **21**, 316A).

[145] E. G. Hammerschmidt, *Ind. Eng. Chem.*, 1934, **26**, 851; *J. Inst. Pet. Tech.*, 1935, **21**, 525A; *Abs.* B, 1934, 948; *Chem. Abs.*, 1934, **28**, 6277. *Oil & Gas J.*, 1935, **34** (5), 34. **87**; *Abs.* B, 1936, 914; *Chem. Abs.*, 1935, **29**, 7046.

The moisture content of liquefied gases such as propane and butane also needs rigid control. One qualitative test for moisture involves the use of cobalt bromide.[146]

TECHNICAL TREATMENT OF CRUDE OIL

Separation of crude oil into component fractions involves distillation followed by refining of individual cuts and, possibly, cracking. Distillation is now carried out in modern pipe stills[147] with capacities up to 20,000 barrels per day. In such operations the oil is preheated continuously in a coil to a temperature sufficiently high to effect vaporization and is then passed into a bubble-plate fractionating tower, the different fractions being simultaneously withdrawn at various points in the tower. In some installations, such as that shown diagrammatically in Fig. 5, the crude is distilled in the first stage at about atmospheric pressure, taking off gasoline, kerosene and gas oil. The residue is subsequently distilled under reduced pressure to furnish lubricating oil fractions. In other installations the entire procedure is carried out in one stage, the lubricating oil being also taken as an overhead product. Indirect heating through the medium of vapors of biphenyl, mercury, or other high-boiling substances is sometimes employed to obviate local overheating and resulting decomposition. Typical fractions are: gasoline, having final boiling (or end) point of about 400°F.; kerosene, end point of 490°F.; light gas oil, final boiling point of 540°F.; mineral seal oil, heavy gas oil, wax distillate and cylinder stock. Enormous technical advances in the large scale distillation of petroleum have been made in the last decade, and the old horizontal shell still, running crude to coke, fuel oil, or lubricating oil, has become of limited value owing to the more economical pipe still.[148]

Refining operations which are used for the subsequent treatment of the individual petroleum fractions are, for the most part, outside the scope of the present work. However, the present chapter contains a brief summary of the salient features of a few solvent extraction processes for the improvement of the higher petroleum fractions (including kerosenes and lubricating oil distillates), since they involve a partial segregation of oil fractions into hydrocarbons of different types. The refining methods of the petroleum industry, which are discussed elsewhere,[149] have for their object the production of petroleum fractions (i.e., complex hydrocarbon mixtures) having properties specially suited for their applications rather than for the separation of pure hydrocarbons or of mixtures of chemically-related hydrocarbons.[150]

STRAIGHT-RUN GASOLINES

Straight-run gasolines consist essentially of a mixture of paraffin, naphthene and aromatic hydrocarbons, unsaturated hydrocarbons being usually present only in small amounts.[151] The relative proportions of these various classes of hydrocarbons in gasolines from different crude oils vary widely.[152] As a rule, however,

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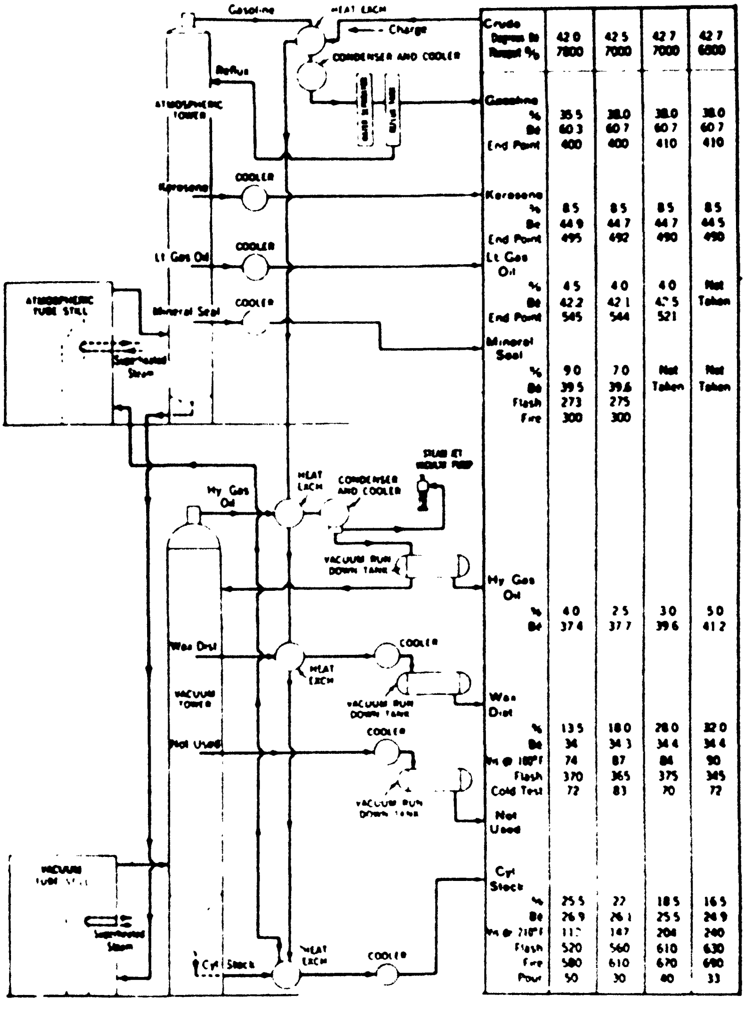
[146] W. H. Bateman, *Refiner*, 1936, **15**, 135; *J. Inst. Pet. Tech.*, 1936, **22**, 295A.

[147] G. R. Hopkins and E. W. Cochrane (Bur. Mines, Information Circ. No. 6850, **1935**; *Chem. Abs.*, 1935, **29**, 8301) give a statistical account of the petroleum refineries, including cracking plants, in the United States on January 1, 1935. For the employment of interfacial tension measurements in refining see E. Vellinger and G. Radulesco, *Ann. combustibles liquides*, 1934, **9**, 279; *Chem. Abs.*, 1934, **28**, 6285.

[148] Petroleum distillation is discussed by J. B. Hill (*Ind. Eng. Chem.*, 1935, **27**, 519; *Chem. Abs.*, 1935, **29**, 3813; *J. Inst. Pet. Tech.*, 1935, **21**, 257A) and by G. Egloff (*Ind. Eng. Chem.*, 1935, **27**, 648; *Chem. Abs.*, 1935, **29**, 4556; *J. Inst. Pet. Tech.*, 1935, **21**, 286A), and the historical development of distillation is described by G. Egloff (*Chem. Met. Eng.*, 1935, **42**, 200; *Chem. Abs.*, 1935, **29**, 3554).

[149] L. Gurwitsch and H. Moore, "The Scientific Principles of Petroleum Technology," D. Van Nostrand Company, Inc., New York, **1932**. V. A. Kalichevsky and B. A. Stagner, "Chemical Refining of Petroleum," The Chemical Catalog Company, Inc., New York, **1933** (A.C.S. Monograph Series). W. L. Nelson, "Petroleum Refinery Engineering," McGraw-Hill Book Company, Inc., New York and London, **1936**.

[150] The instruments used in the control of oil-refining operations and their maintenance have been described by A. C. Proctor and G. Egloff, *Proc. 6th Mid-Year Meeting Am. Petroleum Inst. Sect. III*, 1936, **17M**, 47; *Oil & Gas J.*, 1936, **35** (3), 43, 46, 48, 50; *Refiner*, 1936, **15**, 225; *Chem. Abs.*, 1936, **30**, 7318; *J. Inst. Pet. Tech.*, 1936, **22**, 346A.



Crude Degrees Be [illegible] %	42.0 7800	42.5 7000	42.7 7000	42.7 6800
Gasoline				
%	35.5	38.0	38.0	38.0
Be	60.3	60.7	60.7	60.7
End Point	400	400	410	410
Kerosene				
%	8.5	8.5	8.5	8.5
Be	44.9	44.7	44.7	44.5
End Point	495	492	490	490
Lt Gas Oil				
%	4.5	4.0	4.0	Not Taken
Be	42.2	42.1	42.5	
End Point	545	544	521	
Mineral Seal				
%	9.0	7.0	Not Taken	Not Taken
Be	39.5	39.6		
Flash	273	275		
Fire	300	300		
Hy Gas Oil				
%	4.0	2.5	3.0	5.0
Be	37.4	37.7	39.6	41.2
Wax Dist				
%	13.5	18.0	28.0	32.0
Be	34	34.3	34.4	34.4
Vis @ 100°F	74	87	84	90
Flash	370	365	375	385
Cold Test	72	83	70	72
Not Used				
Cyl Stock				
%	25.5	22	18.5	16.5
Be	26.9	26.1	25.5	24.9
Vis @ 210°F	112	147	204	240
Flash	520	560	610	630
Fire	580	610	670	690
Pour	50	30	40	33

Courtesy Industrial and Engineering Chemistry

FIG. 5.—Diagrammatic Sketch of 2-stage Vacuum-distillation Unit for Pennsylvania Crude. (G. Egloff)

the paraffin hydrocarbons always constitute a considerable proportion of most straight-run gasolines, especially in the lower-boiling fractions.

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[151] The composition of Ural (Perm) petroleum has been discussed by N. D. Zelinski and J. R. Yur'ev (*Brennstoff-Chem.*, 1933, **14**, 347; *Brit. Chem. Abs.* **B**, 1933, 948; *Chem. Abs.*, 1934, **28**, 299) and by D. M. Marko and I. I. Lapkin (*Bull. inst. recherches biol. univ. Perm*, 1932, **8**, 145; *Brit. Chem. Abs.* **B**, 1933, 995; *Chem. Abs.*, 1933, **27**, 4063). A. Sakhanov and R. Virabyantz (*Erdöl u. Teer*, 1933, **9**, 170, 187, 202, 220; *Brit. Chem. Abs.* **B**, 1934, 51) describe the analyses of numerous Russian petroleums, and the properties of North German crude oils are given by G. Keppeler (*Petroleum Z.*, 1933, **29** (37), 6; *Brit. Chem. Abs.* **B**, 1933, 948; *Chem. Abs.*, 1934, **28**, 618). Analyses of Italian petroleums and straight-run gasolines are supplied by A. Campa (*Chim. ind. agr. biol.*, 1933, **9**, 438; *Chem. Abs.*, 1934, **28**, 2167), and Rumanian petroleums and gasolines have been examined by T. Cosciug (*Ann. Sci. univ. Jassy*, 1933, **18**, 118, 415; *Brit. Chem. Abs.* **B**, 1934, 83; *Chem. Abs.*, 1934, **28**, 5641), E. E. Casimer (*Petroleum Z.*, 1934, **30** (44), 1; *Brit. Chem. Abs.* **B**, 1934, 1044; *J. Inst. Pet. Tech.*, 1934, **20**, 567A; *Chem. Abs.*, 1935, **29**, 2700) and by V. Cerchez (*Oel u. Kohle*, 1935, **11**, 474; *J. Inst. Pet. Tech.*, 1935, **21**, 336A; *Chem. Abs.*, 1935, **29**, 8300; *Brit. Chem. Abs.* **B**, 1935, 886).

[152] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

The usual analytical methods suffice to give a rough quantitative picture of the relative proportions of paraffinic, naphthenic and aromatic hydrocarbons in gasolines. The procedure generally adopted involves removal of the aromatics by the aid of sulphuric acid (which exerts a preferential solvent action on these hydrocarbons), followed by a determination of the aniline point of the remainder to ascertain the proportions of paraffinic and naphthenic constituents. The detection and isolation of individual hydrocarbons from gasoline fractions is, however, a much more complicated task and demands elaborate equipment and careful technique.[153]

Prolonged fractionation into relatively narrow cuts is generally adopted as preliminary to the isolation of individual hydrocarbons from gasolines. Much information has been accumulated by the investigations of the Bureau of Mines and A.P.I. Research Projects, and a large number of pure hydrocarbons have been isolated from the gasoline fractions of Mid-Continent crudes.[154] Distillations were carried out in a bubble-cap fractionating column fitted with automatic pressure control. Separations were assisted by the use of reduced pressure (down to 0.0001 mm. mercury) owing to the fact that the vapor pressure-temperature curves of a paraffin and naphthene, normally boiling at similar temperatures, cross each other so that the relative volatilities of these two classes of hydrocarbons can be varied by altering the pressure.[155]

Two types of constant-boiling mixtures were encountered in this work. A group of hydrocarbons having nearly identical boiling points often form a substantially constant-boiling mixture of the "true-solution" class. Such a combination cannot be separated by fractionation. Other types were the azeotropes, having a minimum or maximum boiling point and always associated with the presence of aromatics. Removal of the latter hydrocarbons obviated this formation.[156] In order to break up these constant-boiling mixtures, various methods were employed, including fractional crystallization with or without added solvents, fractionation by extraction with aniline or liquid sulphur dioxide, distillation in the presence of an alcohol or acetic acid or at low pressures and chemical methods such as nitration and sulphonation.

Aromatic hydrocarbons can be separated from gasolines or close-boiling distillates of gasolines by the use of certain selective solvents, such as liquid sulphur dioxide[157] or β,β'-dichlorodiethyl ether.[158] Extraction with 97-99 per cent sulphuric acid is said to eliminate about 90 per cent of the aromatic compounds of which 50-90 per cent can be recovered by dilution of the acid layer and distillation with superheated steam at 140 to 210°C.[159] Fractionation into narrow cuts followed by nitration or bromination has been employed by Cosciug[160] in the examination of the aromatic hydrocarbons in Rumanian petroleums. Separation of pure benzene from a narrow fraction of Shukkoko (Japan) crude oil has been achieved by Mizuta[161] by repeated fractionation and crystallization at low temperatures. It has been found by Mair and White[162] that silica gel exercises a preferential adsorptive power towards aromatic and olefinic hydrocarbons, which can thus be removed from paraffin and naphthene hydrocarbons. The gel shows a slight tendency to adsorb naphthenes in preference to paraffin hydrocarbons, while a slight separation of *n*-paraffins of different molecular weights was also observed. This same agent has been employed to remove aromatic hydrocarbons from ethylcyclohexane isolated from petroleum.[163] The use of various adsorbents in the purification and refining of petroleum products has been investigated by Dubrisay.[163a]

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[153] See also Chapter 50.

[154] R. T. Leslie and J. D. White, *J. Research Natl. Bur. Standards*, 1935, **15**, 211 (Research Paper 824); *Chem. Abs.*, 1935, **29**, 8300; *J. Inst. Pet. Tech.*, 1935, **21**, 448A. E. W. Washburn, *Am. Petroleum Inst. Proc. 14th Ann. Meeting*, 1933, **14** (3), 111; *Chem. Abs.*, 1934, **28**, 3877; *J. Inst. Pet. Tech.*, 1934, **20**, 308A. F. D. Rossini, *Oil & Gas J.*, 1935, **33** (52), 61, 62, 64, 73; *Chem. Abs.*, 1935, **29**, 6410; *J. Inst. Pet. Tech.*, 1935, **21**, 256A.

[155] The advantages of the use of high vacuum in distillation, particularly as regards less cracking and olefin formation, are described by N. Danaila and R. Verona (*Bul. chim. soc. române chim.*, 1932, **35**, 37; *Chem. Abs.*, 1934, **28**, 3567; *Brit. Chem. Abs.* **B**, 1934, 438; *J. Inst. Pet. Tech.*, 1934, **20**, 239A).

[156] The existence, at atmospheric pressure, of a constant-boiling mixture of acetylene and ethane has been reported by W. A. McMillan (*J. A. C. S.*, 1936, **58**, 1345; *Chem. Abs.*, 1936, **30**, 6702; *J. Inst. Pet. Tech.*, 1936, **22**, 436A).

[157] For example, see V. T. Cerchez, *Bull. Soc. Chim. România*, 1934, **16**, 31; *Brit. Chem. Abs.* **B**, 1936, 6.

[158] F. Galle, R. Klatt and W. Friedl, *Petroleum Z.*, 1935, **31** (36), 1; *J. Inst. Pet. Tech.*, 1935, **21**, 405A; *Chem. Abs.*, 1936, **30**, 1356; *Brit. Chem. Abs.* **B**, 1935, 980.

[159] R. A. Virobyantz, *Neft. Khoz.*, 1933, **25**, 160; *Chem. Abs.*, 1934, **28**, 3227; *Brit. Chem. Abs.* **B**, 1934, 820; *J. Inst. Pet. Tech.*, 1934, **20**, 415A.

Segregation of naphthenes from paraffin hydrocarbons is a matter of considerable difficulty. Certain selective solvents have been suggested, some of which are discussed later in this chapter. According to Galle, Klatt and Friedl[164] no separation is effected by the use of β,β'-dichlorodiethyl ether. Low temperature fractional crystallization from a mixture of liquid propane and methane[165] and also from dichlorodifluoromethane[166] has been advocated particularly for the isolation of pure naphthenes from gasoline fractions also containing paraffins. Glacial acetic acid has been employed effectively in operations involving fractional distillation.[167] Five- and six-membered naphthenes in straight-run gasolines can be identified and determined by catalytic dehydrogenation (to the corresponding aromatics) in the presence of platinum or palladium, according to the Zelinskii method.[168] An analogous procedure has been applied to various fractions of Surakhany gasoline by Zelinskii and Shuykin,[169] using nickel and platinum catalysts.

Paraffin Hydrocarbons in Gasoline Fractions. For the isolation of normal paraffin hydrocarbons from admixtures with isoparaffins, advantage is often taken of the superior chemical activity of the latter (particularly those containing a tertiary carbon atom) towards such reagents as chlorosulphonic acid, antimony pentachloride and nitric acid. The isolation of the normal paraffins, hexane to decane, from fractions of various Russian gasolines was accomplished by Virobyantz and Gabrielyantz[170] by employing 98 per cent sulphuric acid (to eliminate more reactive hydrocarbons), followed by repeated treatments with chlorosulphonic acid at temperatures ranging from 55°C. in the case of hexane to 105°C. for octane, nonane and decane. In the preparation of *n*-heptane from a shale oil gasoline, Orlov and Ivanov[171] employed antimony pentachloride, a reagent known to attack tertiary paraffins at ordinary temperatures. The same reagent has been employed to identify tertiary paraffins in Surakhany straight-run gasoline, but the reaction is said to be inapplicable for exact analysis.[172]

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[160] T. Cosciug, *Ann. Sci. univ. Jassy*, 1933, **18**, 118 415; *Chem. Abs.*, 1934, **28**, 5641, *Brit. Chem. Abs.* **B**, 1934, 83

[161] M. Mizuta, *J. Soc. Chem. Ind., Japan*, 1933, **36**, Suppl. Bind., 448; *Brit. Chem. Abs.* **B**, 1933, 900; *Chem. Abs.*, 1934, **28**, 301.

[162] B. J. Mair and J. D. White, *J. Research Natl. Bur. Standards*, 1935, **15**, 51; *J. Inst. Pet. Tech.*, 1935, **21**, 447A; *Brit. Chem. Abs.* **B**, 1935, 886.

[163] F. W. Rose, Jr., and J. D. White, *J. Research Natl. Bur. Standards*, 1935, **15**, 151, *Chem. Abs.*, 1935, **29**, 7623; *Brit. Chem. Abs.* **B**, 1935, 1030; *J. Inst. Pet. Tech.*, 1935, **21**, 447A.

[163a] R. Dubrisay, *Ann. combustibles liquides*, 1933, **8**, 607, *Chem. Abs.*, 1934, **28**, 620, *Brit. Chem. Abs.* **B**, 1934, 996.

[164] E. Galle, R. Klatt and W. Friedl, *Petroleum Z.*, 1935, **31** (36), 1; *J. Inst. Pet. Tech.*, 1935, **21**, 405A; *Chem. Abs.*, 1936, **30**, 1356; *Brit. Chem. Abs.* **B**, 1935, 980.

[165] R. T. Leslie, *J. Research Natl. Bur. Standards*, 1935, **15**, 41; *J. Inst. Pet. Tech.*, 1935, **21**, 447A; *Brit. Chem. Abs.* **B**, 1935, 887; *Chem. Abs.*, 1935, **29**, 6740. F. W. Rose, Jr., and J. D. White, *J. Research, Natl. Bur. Standards*, 1935, **15**, 151; *Brit. Chem. Abs.* **B**, 1935, 1030; *J. Inst. Pet. Tech.*, 1935, **21**, 447A; *Chem. Abs.*, 1935, **29**, 7623

[166] J. D. White and F. W. Rose, Jr., *J. Research Natl. Bur. Standards*, 1934, **13**, 799; *Brit. Chem. Abs.* **B**, 1935, 293; *Chem. Abs.*, 1935, **29**, 3145; *J. Inst. Pet. Tech.*, 1935, **21**, 160A.

[167] S. T. Schicktanz, Paper presented before the Petroleum Division of the A.C.S. at Pittsburgh on Sept. 7-11, 1936.

[168] A. N. Sakhanov, A. I. Doladugin and I. M. Egorova, *Gosudarstvennoe Nauch.-Tekh. Izdatelstvo Moscow Petrograd*, **1931**, 175; *Chem. Abs.*, 1934, **28**, 297.

[169] N. D. Zelinskii and N. I. Shuikin, *Bull. acad. sci. U.R.S.S.*, **1935**, 229; *Ind. Eng. Chem.* 1935, **27**, 1209; *Chem. Abs.*, 1936, **30**, 601; *Brit. Chem. Abs.* **B**, 1935, **1081**; *J. Inst. Pet. Tech.*, 1935, **21**, 448A.

[170] R. A. Virobyantz and S. M. Gabrielyantz, *Neft. Khoz.*, 1933, **25**, 158; *Chem. Abs.*, 1934, **28**, 4878. For the preparation of several crystalline aliphatic hydrocarbons see J. Strating, H. J. Backer, J. Lolkema, *Rec. trav. chim.*, 1936, **55**, 903; *Chem. Abs.*, 1937, **31**, 1000.

A method for the examination of gasolines by the aid of their Raman spectra[173] has been proposed by Andant.[174] This method does not permit the immediate identification of all the hydrocarbons present in a gasoline, owing to the similarity of the spectra of hydrocarbons of the same group. However, it often leads to a precise knowledge of the chemical groups present. By applying this procedure, Andant[175] examined several gasolines and obtained evidence that paraffins, naphthenes and aromatics were present, the proportions depending upon the particular gasoline considered. The near infra-red absorption spectra of a number of pure hydrocarbons have been studied by Liddel and Kasper.[176]

Of the paraffin hydrocarbons, the following have been shown to be present in a distillate, boiling between 55 and 145°C., of an Oklahoma petroleum: 2,3-dimethylbutane, 2- and 3-methylpentane, *n*-hexane, 2,2-dimethylpentane, 2-methylhexane, *n*-heptane, 2-methylheptane, *n*-octane. From the portion boiling between 145 and 180°C. of the same petroleum, *n*-nonane and *n*-decane were isolated.[177] The normal paraffins from hexane to decane have been isolated from appropriate fractions of Grozny mixed-base and Maikop gasolines by Virobyantz and Gabrielyantz,[178] and *n*-hexane and *n*-heptane, with some cycloparaffins and aromatics, have been identified in Hodonin (Czechoslovakia) crude oil by Landa, Machacek and Mzourek.[179] By careful fractionation and examination of the various cuts, Tongberg, Quiggle and Fenske[180] have shown that Michigan straight-run gasoline contained a greater proportion of *n*-paraffins and aromatics than Pennsylvania straight-run gasoline. The latter, however, is richer in branched-chain paraffins. According to Leslie,[181] 2-methylheptane and iso-octane are present in a fraction (of a Mid-Continent petroleum) which boiled between 115 and 124°C. Nonane (and 2-nonene) has been isolated from a cut of Fushun shale oil distilling at 133-

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[171] N. A. Orlov and I. Z. Ivanov, *Khim. Tverdogo Topliva*, 1934, 5, 788; *J. Inst. Pet. Tech.*, 1936, **22**, 88A; *Chem. Abs.*, 1935, **29**, 7628; *Brit. Chem. Abs.* **B**, 1936, 1188.

[172] P. Panyutin and E. Firsanova, *Khim. Tverdogo Topliva*, 1935, 7, 801.

[173] A detailed account of the application of Raman effect in petroleum chemistry is given by J. Hibben, *Ind. Eng. Chem.*, 1934, **26**, 646; *Chem. Abs.*, 1934, **28**, 4311; *Brit. Chem. Abs.* **B**, 1934, 662; *J. Inst. Pet. Tech.*, 1934, **20**, 483A. For illustrations concerning the use of Raman spectra in petroleum analysis, see Chapter 50.

[174] A. Andant, *Chim. & ind.*, 1933, **29**, Spec. No., 480; *Brit. Chem. Abs.* **B**, 1934, 132.

[175] A. Andant, *Chim. & ind.*, 1933, **30**, 1011; *Chem. Abs.*, 1934, **28**, 2170.

[176] U. Liddel and C. Kasper, *J. Research Natl. Bur. Standards*, 1933, **11**, 599; *J. Inst. Pet. Tech.*, 1934, **20**, 308A; *Chem. Abs.*, 1934, **28**, 1601; *Brit. Chem. Abs.* **A**, 1934, 238.

[177] R. T. Leslie and J. D. White, *J. Research Natl. Bur. Standards*, 1935, **15**, 211; *Chem. Abs.*, 1935, **29**, 8300; *J. Inst. Pet. Tech.*, 1935, **21**, 448A.

[178] R. A. Virobyantz and S. M. Gabrielyantz, *Neft. Khoz.*, 1933, **25**, 158; *Chem. Abs.*, 1934, **28**, 4878.

[179] St. Landa, V. Machaček and J. Mžourek, *Petroleum Z.*, 1934, **30** (16), 1; *J. Inst. Pet. Tech.*, 1934, **20**, 358A; *Chem. Abs.*, 1934, **28**, 4873.

[180] C. O. Tongberg, D. Quiggle and M. R. Fenske, *Ind. Eng. Chem.*, 1936, **28**, 201; *Chem. Abs.*, 1936, **30**, 2736; *J. Inst. Pet. Tech.*, 1936, **22**, 156A; *Brit. Chem. Abs.* **B**, 1936, 307. Small scale fractionating equipment has been described by H. T. Rall and H. M. Smith (Ind. *Eng. Chem.*, *Anal. Ed.*, 1934, **6**, 373; *Brit. Chem. Abs.* **B**, 1934, 1044; *Chem. Abs.*, 1934, **28**, 7496; *J. Inst. Pet. Tech.*, 1935, **21**, 50A), C. O. Tongberg, D. Quiggle and M. R. Fenske (*Ind. Eng. Chem.*, 1934, **26**, 1213; *J. Inst. Pet. Tech.*, 1934, **20**, 609A; *Brit. Chem. Abs.* **A**, 1935, 59; *Chem. Abs.*, 1935, **29**, 1), M. R. Fenske, C. O. Tongberg, D. Quiggle and D. S. Cryder (*Ind. Eng. Chem.*, 1936, **28**, 644; *Chem. Abs.*, 1936, **30**, 4725; *J. Inst. Pet. Tech.*, 1936, **22**, 442A; *Brit. Chem. Abs.* **B**, 1936, 768) and A. Rose (*Ind. Eng. Chem.*, 1936, **28**, 1210; *Chem. Abs.*, 1936, **30**, 7389).

[181] R. T. Leslie, Paper presented before the Petroleum Division of the A.C.S. at Pittsburgh on Sept. 7-11, 1936. *J. Research Natl. Bur. Standards*, 1936, **17** (5), 761.

[illegible] C.[182] 3,3-Dimethylheptane and 3,3-diethylpentane are believed to exist in minor proportions in this latter distillate. White and Rose[183] have utilized glacial acetic acid in the separation of an isononane from an Oklahoma petroleum by fractional distillation.

Naphthenic Hydrocarbons in Gasoline Distillates. The monocyclic naphthenes in straight-run gasolines are usually mixtures of both cyclopentane and cyclohexane hydrocarbons. Evidence for the occurrence of cycloparaffins with three- or four-membered rings is lacking although the presence of cycloheptane hydrocarbons in some petroleums has been inferred from spectroscopic data.[184] The relative proportions of cyclohexane and cyclopentane hydrocarbons in a number of Russian straight-run gasolines have been determined by Sakhanov, Doladugin and Egorova,[185] using the catalytic dehydrogenation method of Zelinskii. In practically all the crude oils investigated, the maximum content of cyclohexane homologues occurred in the fraction boiling at 95-122°C. The gasoline fractions of Baku crude oil contained up to 50 per cent of cyclohexanes, which was greater than that of cyclopentanes.

Zelinskii and Schuykin[186] observed that fractions of Surakhany gasoline (boiling between 75 to 105°C. and 105 to 125°C.) contained about 53 per cent (by volume) of hydroaromatic hydrocarbons which could be dehydrogenated (over nickel deposited on alumina) to aromatics. Higher-boiling cuts, up to 140°C., also possessed a large proportion of hexamethylene (and other naphthene or cyclane) derivatives. Analyses of the latter fractions, as given by these investigators, are in Table 7. The toluene fraction, boiling at 100.5-110.5°C., of Maikop gasoline was found by Maslov and Kozuireva[187] to contain 33 per cent of cyclohexanes and 21 per cent of cyclopentane hydrocarbons. Leslie[188] reports the presence of two octanaphthenes in the fraction of a Mid-Continent petroleum distilling between 115 and 124°C. In the portions of Ural (Perm) petroleum boiling at 150-240°C., examined by Zelinskii and Yur'ev,[189] the proportion of cyclohexane hydrocarbons was about the same throughout, but the content of saturated cyclic compounds increased with the boiling range.

TABLE 7.—*Analysis of Fractions of Surakhany Gasoline.*

	Per Cent by Weight			
B. P. of Fraction °C.	Aromatic Hydrocarbons	Cyclohexane Hydrocarbons	Other Cyclanes	Paraffins
118-120	About 1.0	56.2	15.5	27.3
120-124	1.7	56.9	15.7	25.7
124-130	4.0	54.3	20.0	21.7
130-140	5.0	44.6	23.2	27.2

Of the five-membered naphthenes, cyclopentane has been found in Hodonin

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[182] F. Horie, *J. Soc. Chem. Ind., Japan*, 1936, **39**, Suppl. Bind., 140; *Chem. Abs.*, 1936, **30**, 5399; *Brit. Chem. Abs.* **B**, 1936, 626.

[183] J. D. White and F. W. Rose, Jr., Paper presented before the Petroleum Division of the A.C.S. in Pittsburgh on Sept. 7-11, 1936. *J. Research Natl. Bur. Standards*, Research Paper 955, 1936, **17**, 943.

[184] A. Andant, *Chim. & ind.*, 1933, **30**, 1011; *Chem. Abs.*, 1934, **28**, 2170.

[185] A. N. Sakhanov, A. I. Doladugin and I. M. Egorova, *Gosudarstvennoe Nauch.-Tekh. Izdatelstvo Moscow-Petrograd*, **1931**, 175; *Chem. Abs.*, 1934, **28**, 297.

[186] N. D Zelinskii and N. I. Shuikin, *Bull. acad. sci. U.R.S.S.*, **1935**, 229; *Ind. Eng. Chem.*, 1935, **27**, 1209; *Chem. Abs.*, 1936, **30**, 601; *Brit. Chem. Abs.* **B**, 1935, 1081; *J. Inst. Pet. Tech.*, 1935, **21**, 448A.

[187] P. S. Maslov and E. I. Kozuireva, *Groznenskii Neftyanik*, 1934, **4** (8), 59; *Chem. Abs.*, 1935, **29**, 2716; *Brit. Chem. Abs.* **B**, 1935, 1031.

[188] R. T. Leslie, Paper presented before the Petroleum Division of the A.C.S. in Pittsburgh on Sept. 7-11, 1936. *J. Research Natl. Bur. Standards*, Research Paper 943, 1936, **17**, 761.

[189] N. D. Zelinskii and Y. K. Yur'ev, *Brennstoff-Chem.*, 1933, **14**, 347; *Chem. Abs.*, 1934, **28**, 299; *Brit. Chem. Abs.* **B**, 1933, 948.

(Czechoslovakia) petroleum.[190] Methylcyclopentane and dimethylcyclopentane have been isolated from Oklahoma straight-run gasoline[191] and recognized in Montechino (Italy) crude oils.[191a] The nonanaphthene, boiling at 136.65°C., extracted from an Oklahoma crude oil by White and Rose,[192] is considered likely to be a cyclopentane derivative.

Cyclohexane has been identified as a constituent of the crude oil of Montechino[193] and of Mid-Continent petroleum.[193a] It is also present, along with methylcyclohexane and dimethylcyclohexanes, in Hodonin petroleum[194] and in Surakhany (Russia) straight-run gasoline.[195] The dimethylcyclohexane obtained by Leslie[196] by fractional distillation and crystallization of the fraction, boiling near 120.5°C., of a Mid-Continent petroleum was mainly the meta-compound admixed with a little of the para form. A portion of Surakhany gasoline boiling between 115 and 125°C. was stated to contain 1,2-, 1,3- and 1,4-dimethylcyclohexane.[196a] A fraction of Baku petroleum which boiled in the range of 135-138°C. was said to furnish 1,2- and 1,3-dimethylcyclohexane as well as 1-methyl-2-ethyl, 1-methyl-3-ethyl and 1,2,4-trimethylcyclohexane.[196b] Ethylcyclohexane has been obtained from the same petroleum by a laborious procedure involving repeated fractional distillation, crystallization from propane and methane, filtration through silica gel and distillation with acetic acid.[197] The existence of 1,3-5-trimethylcyclohexane in Hodonin (Czechoslovakia) oil is reported.[198]

Aromatic Hydrocarbons in Gasoline. Aromatic hydrocarbons so far identified in Mid-Continent straight-run gasolines are benzene, toluene, ethylbenzene, *o*-, *m*- and *p*-xylenes and the three trimethylbenzenes.[199] Benzene, xylene, mesitylene and naphthalene have been found in the gasoline fractions of Hodonin (Czechoslovakia) petroleum.[200] Benzene, which is also present in some Italian petroleums,[201] has been isolated in pure form from Schukkoko (Japan) crude oil by Mizuta[202] and from a Grozny petroleum fraction boiling below 105°C.[203] Fractionation of a toluene fraction of the latter petroleum in a discontinuous fractionating column furnished toluene of about 50 per cent purity. It was believed that a purity of 70 per cent should be possible with 25 actual plates.[204] The presence of

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[190] St. Landa, V. Macháček and J. Mžourek, *Petroleum Z.*, 1934, **30** (16), 1; *J. Inst. Pet. Tech.*, 1934, **20**, 358A; *Chem. Abs.*, 1934, **28**, 4873.

[191] R. T. Leslie and J. D. White, *J. Research Natl. Bur. Standards*, 1935, **15**, 211; *Chem. Abs.*, 1935, **29**, 8300; *J. Inst. Pet. Tech.*, 1935, **21**, 448A.

[191a] A. Campa, *Chim. ind. agr. biol.*, 1933, **9**, 438; *Chem. Abs.*, 1934, **28**, 2167.

[192] J. D. White and F. W. Rose, Jr., *J. Research Natl. Bur. Standards*, 1934, **13**, 799; *J. Inst. Pet. Tech.*, 1935, **21**, 160A; *Brit. Chem. Abs.* **B**, 1935, 293; *Chem. Abs.*, 1935, **29**, 3145.

[193] A. Campa, *loc. cit.*

[193a] R. T. Leslie, *loc. cit.*

[194] St. Landa, V. Macháček and J. Mžourek, *loc. cit.*

[195] P. Panyutin and E. Firsanova, *Khim. Tverd. Topliva*, 1935, **7**, 801.

[196] R. T. Leslie, *J. Research Natl. Bur. Standards*, 1935, **15**, 41; *Brit. Chem. Abs.* **B**, 1935, 887; *Chem. Abs.*, 1935, **29**, 6740; *J. Inst. Pet. Tech.*, 1935, **21**, 447A.

[196a] B. A. Kazanskii and M. I. Markosova, *J. Gen. Chem.* (*U.S.S.R.*), 1936, **6**, 884; *Chem. Abs.*, 1936, **30**, 6930; *Brit. Chem. Abs.* **B**, 1936, 916; *Chem. Zentr.*, 1936, **2**, 3035.

[196b] B. A. Kazanskii and M. P. Eliseeva, *J. Gen. Chem.* (*U.S.S.R.*), 1936, **6**, 888; *Chem. Abs.*, 1936, **30**, 6930; *Brit. Chem. Abs.* **B**, 1936, 916; *Chem. Zentr.*, 1936, **2**, 3035.

[197] F. W. Rose, Jr., and J. D. White, *J. Research Natl. Bur. Standards*, 1935, **15**, 151; *J. Inst. Pet. Tech.*, 1935, **21**, 447A; *Chem. Abs.*, 1935, **29**, 7623; *Brit. Chem. Abs.* **B**, 1935, 1030.

[198] St. Landa, V. Macháček and J. Mžourek, *Petroleum Z.*, 1934, **30** (16), 1; *J. Inst. Pet. Tech.*, 1934, **20**, 358A; *Chem. Abs.*, 1934, **28**, 4873.

[199] R. T. Leslie and J. D. White, *J. Research Natl. Bur. Standards*, 1935, **15**, 211; *Chem. Abs.*, 1935, **29**, 8300; *J. Inst. Pet. Tech.*, 1935, **21**, 448A. For the influence of the structure of aromatic hydrocarbons in lubricating oil see N. I. Chernozhukov, *Neft. Khoz.*, 1935, **29** (9), 72; *Chem. Abs.*, 1936, **30**, 8589; *J. Inst. Pet. Tech.*, 1937, **23**, 21A.

[200] St. Landa, V. Macháček and J. Mžourek, *loc. cit.*

[201] A. Campa, *Chim. ind. agr. biol.*, 1933, **9**, 438; *Chem. Abs.*, 1934, **28**, 2167.

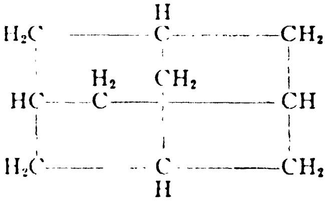
[202] M. Mizuta, *J. Soc. Chem. Ind., Japan*, 1933, **36**, Suppl. bind., 448; *Chem. Abs.*, 1934, **28**, 301; *Brit. Chem. Abs.* **B**, 1933, 900.

[203] V. Markovnikoff, *J. Russ. Phys. Chem. Soc.*, 1902, **34**, 635; *J.C.S.*, 1903, **84**, 19.

[204] M. Mizuta, *J. Soc. Chem. Ind., Japan*, 1935, **38**, Suppl. bind., 21; *Brit. Chem. Abs.* **B**, 1935, 392.

m-xylene in a low boiling cut of a Fushun shale oil has been shown.[205] Mizuta[206] has separated *o*- and *p*-nitrotoluene from mononitrotoluene prepared from the gasoline fraction of Shukkoko crude oil. Also, from the same crude, ethylbenzene and the three xylenes were isolated.[207] Cosciug[208] has identified the following aromatic hydrocarbons in the fraction, boiling at 40-200°C. at 27-28 mm., of Rumanian petroleum: toluene, the three xylenes, 1,3,5-trimethylbenzene, 1,3-methylethylbenzene, *ter.*-butylbenzene, pseudocumene, 1,2,3,4- and 1,2,4,5-tetramethylbenzenes. The distribution of aromatic hydrocarbons in several Rumanian gasolines has been studied by Cerchez.[209]

An interesting hydrocarbon, adamantane, has been isolated from Hodonin (Czechoslovakia) crude oil fractions. Its structural formula, shown below, indicates it to be probably the lowest member of a series belonging to the tricyclodecane group.[210]



KEROSENES

The most important characteristic of kerosenes is their burning quality, a property which is adversely affected by the presence of asphaltic compounds, sulphur and halogen compounds. An increase in the illuminating power of kerosenes results from increasing aromatic hydrocarbon content. Treatment of kerosenes for the removal of these deleterious constituents has been described by Critchley,[211] the usual refining agents being sulphuric acid or liquid sulphur dioxide. Fuming sulphuric is recommended for asphaltic kerosenes, but weaker acids are sufficient for the paraffin-base oils. In the Edeleanu process involving solvent extraction with liquid sulphur dioxide at low temperatures, the dioxide exerts a preferential solvent action on aromatic and unsaturated hydrocarbons as well as on sulphur compounds (including mercaptans, disulphides and cyclic sulphur-containing bodies). Most paraffin hydrocarbons are practically insoluble in this solvent. The color reversion often encountered in kerosenes may be caused by oxidation of phenolic constituents and probably cyclopentadiene and unsaturated naphthenes. In some instances, particularly with unrefined kerosenes, amino compounds may also be involved. The sulphur dioxide extract, obtained as described above, may be hydrogenated to furnish a solvent for insecticidal compositions.[211a] The extract, when freed from the dioxide, is said to have a solvent power of 2.3 per cent for rotenone and rotenoids. Hydrogenation is reported to increase the solvent action to 7.2 per cent.

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[205] F. Horie, *J. Soc. Chem. Ind., Japan*, 1936, **39**, Suppl. bind., 140; *Chem. Abs.*, 1936, **30**, 5399; *Brit. Chem. Abs.* **B**, 1936, 626.

[206] M. Mizuta, *J. Soc. Chem. Ind., Japan*, 1935, **38**, Suppl. bind., 629; *Brit. Chem. Abs.* **B**, 1936, 181; *Chem. Abs.*, 1936, **30**, 1548.

[207] M. Mizuta, *J. Soc. Chem. Ind., Japan*, 1936, **39**, Suppl. bind. 258; *Chem. Abs.*, 1936, **30**, 8586; *Brit. Chem. Abs.* **B**, 1936, 1077. *J. Soc. Chem. Ind., Japan*, 1936, **39**, Suppl. bind. 311; *Chem. Abs.*, 1937, **31**, 528.

[208] T. Cosciug, *Ann. sci. univ. Jassy*, 1933, **18**, **118**, 415; *Brit. Chem. Abs.* **B**, 1934, 83; *Chem. Abs.*, 1934, **28**, 5641.

[209] V. T. Cerchez, *Bul. Soc. Chim. România*, 1934, **16**, 31; *Brit. Chem. Abs.* **B**, 1936, 6. *Oel u. Kohle*, 1935, **11**, 474; *Brit. Chem. Abs.* **B**, 1935, 886; *J. Inst. Pet. Tech.*, 1935, **21**, 336A; *Chem. Abs.*, 1935, **29**, 8300.

[210] St. Landa, V. Macháček and J. Mžourek, *loc. cit.* See also St. Landa, V. Macháček, J. Mžourek and Mme. Landa, *Chim. & ind.*, Special No., 1933, **29**, 506; *Chem. Abs.*, 1933, **27**, 5949; *Brit. Chem. Abs.* **B**, 1934, 132.

[211] G. N. Critchley, *Fuel*, 1934, **13**, 314; *J. Inst. Pet. Tech.*, 1934, **20**, 577A; *Brit. Chem. Abs.* **B**, 1934, 1092; *Chem. Abs.*, 1934, **28**, 7491.

The presence of naphthene hydrocarbons in kerosene distillates has been shown by the work of Wenzel and Weiser, previously mentioned. These investigators prepared cuts of narrow boiling ranges and corresponding to hydrocarbons having 13 to 28 carbon atoms per molecule, and studied the oxidation products therefrom. As pointed out before, Zelinskii[212] obtained evidence for the occurrence of cyclohexane derivatives (by dehydrogenation of kerosene fractions) and also of paraffins. The isolation of pseudocumene, mesitylene and hemimellitine from the sulphur-dioxide extract of kerosene (from Oklahoma crude oil) is described by Mair and Schicktanz.[213]

The kerosene fraction, boiling between 150 and 250°C., of a Ural crude oil has been shown by Zelinskii[214] to contain monosubstituted aromatic compounds in the 225-240°C. cut, but not any trace of decahydronaphthalene. Naphthalene and β-methylnaphthalene have been obtained from Rumanian oil fractions boiling between 100 and 112°C. by treatment with a concentrated ethereal solution of picric acid, causing the picrates of these hydrocarbons to be precipitated.[215]

HIGHER PETROLEUM FRACTIONS

Although the lubricating oil fractions of petroleum have received intensive study from the viewpoint of their physico-chemical characteristics, including viscosity-temperature relationship, oiliness and susceptibility to oxidation, very little advance has been made in the knowledge of their chemical nature. However, the preliminary results of an investigation of the characteristics of the hydrocarbons in lubricating oil fractions of Oklahoma petroleum is reported by Mair, Schicktanz and Rose.[216] The distillates were extracted with liquid sulphur dioxide, crystallized from ethylene chloride and fractionally distilled in order to separate asphaltic and resinous matter, wax and water-white fractions, respectively. It appears likely from the results obtained that this oil can be separated by distillation into constant boiling fractions which can be separated, in turn, into hydrocarbons of different types by one of the other physical methods available.

The aromatic constituents, extracted from an American asphalt-base spindle oil by liquid sulphur dioxide and subsequently fractionated under reduced pressure, have been studied by Zerbe and Folkens.[217] Examination of the absorption spectra of the fractions showed that those of lower boiling point consisted of substituted derivatives of naphthalene (and possibly benzene) and those of higher boiling

[211a] L. A. Mikeska, U. S. P. 2,066,184, Dec. 29, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1937, **31**, 1151.

[212] N. D. Zelinskii, *Foreign Petroleum Tech.*, 1933, 1, 27, 51; *Chem. Abs.*, 1934, **28**, 1177; *Brit. Chem. Abs.* **B**, 1934, 486.

[213] B. J. Mair and S. T. Schicktanz, *J. Res. Natl. Bur. Standards*, 1933, 11, 665; *Chem. Abs.*, 1934, **28**, 1847.

[214] N. D. Zelinskii, *Acad of Sci. of U.S.S.R. Trans. of the June Session dealing with the problems of the Ural-Kuznetzk district, Petrograd*, **1932**; *Foreign Petroleum Tech.*, 1933, 1, 27, 51; *Chem. Abs.*, 1934, **28**, 1177; *Brit. Chem. Abs.* **B**, 1934, 486.

[215] T. Cosciug, *Petroleum Z.*, 1935, **31** (41), 5; *Brit. Chem. Abs.* **B**, 1935, 1081; *J. Inst. Pet. Tech.*, 1935, **21**, 446A; *Chem. Abs.*, 1936, **30**, 2733.

[216] B. J. Mair, S. T. Schicktanz and F. W. Rose, Jr., *J. Research Natl. Bur. Standards*, 1935, 15, 557; *Chem. Abs.*, 1936, **30**, 1985. B. J. Mair and S. T. Schicktanz, *Ind. Eng. Chem.*, 1936, **28**, 1446; *Chem. Abs.*, 1937, **31**, 1188. *J. Research Natl. Bur. Standards*, Research Paper 953, 1936, 17, 909. See also E. W. Washburn, *Nat. Pet. News*, 1933, **25** (51, 29; *J. Inst. Pet. Tech.*, 1934, **20**, 171A. M. R. Cannon and M. R. Fenske (Paper presented before the Petroleum Division of the A.C.S. at Pittsburgh on Sept. 7-11, 1936) have shown in a general way the types of products obtainable by a combination of distillation and solvent extraction processes as applied to the study of the composition of lubricating oil fractions.

[217] C. Zerbe and K. Folkens, *Brennstoff-Chem.*, 1935, **16**, 161, 208; *Brit. Chem. Abs.* **B**, 1935 615; *J. Inst. Pet. Tech.*, 1935, **21**, 300A; *Chem. Abs.*, 1935, **29**, 5643.

points were derived from phenanthrene and higher polycyclic aromatics. This was also confirmed by the production of the parent aromatic hydrocarbons (benzene and naphthalene) by controlled pyrolysis. The latter operation was effected in a tinned iron tube in the presence of hydrogen, de-alkylation being apparently an important reaction under these conditions.

The oiliness, or friction-reducing, property of natural lubricating oils has been subject of much investigation,[218] but it is still uncertain to what extent this characteristic is dependent upon non-hydrocarbon materials present in the oil. Wardner[219] extracted petrolatum and lubricating oil from Pennsylvania long residuum[220] with acetone and obtained insoluble portions which he termed "proto-petrolatum" or "proto-oil," having highly developed lubricating properties and consisting of unctuous, viscous hydrocarbons of high molecular weight. It was thought by Wardner that these hydrocarbons might be responsible for the accredited "oiliness" of Pennsylvania oils.

A number of workers have attempted to correlate various data on the physical properties of lubricating oils. For example, Keith and Roess[221] prepared a series of curves with which the molecular weight of higher petroleum fractions may be predicted from a knowledge of their viscosities at 100°F. and 210°F. Mair and Willingham[222] noted that the solubility relations of derivatives of monocyclic aromatic hydrocarbons are similar to those of naphthenes with 5 or 6 rings per molecule. With this in mind, Mair and Willingham believe that if such aromatics are present in the lubricant fraction, solvent extraction processes (known or used up to 1936) are discarding these along with the less desirable naphthenes. This topic is, according to these investigators, also of practical importance because such aromatics have viscosity characteristics as good as the best naphthenes besides possessing desirable oxidation qualities.

From their observations, Dunstan and Thole[223] state that the true lubricant is an unsaturated compound; and, they maintain that unsaturation has, in general, the effect of raising viscosity. Their belief is that a lubricating oil should contain a certain proportion of unsaturated hydrocarbons and as large a proportion as is compatible with not too much susceptibility to oxidation, polymerization, gumming and reactivity. Wiggins[224] reviewed the available data on the chemical constitution of hydrocarbons and concluded that the aliphatic hydrocarbons have low viscosities in relation to the number of carbon atoms in the molecule, and that the viscosity-temperature stability increases with chain-length and decreases with branching. Hydrocarbons containing simple cyclic structures have higher viscosities, for a given molecular weight, and also good viscosity-temperature characteristics; whereas, the introduction of polycyclic groups markedly increases the viscosity but reduces the viscosity-temperature stabilities.

[218] S. Kyropoulos, *Physik. Z.*, 1928, **29**, 942; *Chem. Abs.*, 1929, **23**, 1794; *Z. physik Chem.*, 1929, **144**, 22; *Chem. Abs.*, 1930, **24**, 3351. *World Petroleum Congress*, 1933 **2**, 391; *Brit. Chem. Abs.* **B**, 1934, 915. *Refiner*, 1936, **15**, 269; *J. Inst. Pet. Tech.*, 1936, **22**, 453A. O. Bridgeman, *Physics*, 1934, **5**, 125; *Chem. Abs.*, 1934, **28**, 4888. M. Nottage, *Dept. Sci. Ind. Research, Lubrication Research, Tech. Paper No. 2*, **1934**; *Brit. Chem. Abs.* B, 1935, 212. Reviews of lubricants and lubrication have been contributed by A. R. Bowen (*J. Inst. Pet. Tech.*, 1934, **20**, 419; *J. Inst. Pet. Tech.*, 1934, **20**, 408A) and S. I.M. Auld (*J. Inst. Pet. Tech.*, 1935 **21**, 379; *J. Inst. Pet. Tech.*, 1935, **21**, 308A).

[219] G. A. Wardner, *Oil & Gas J.*, 1934, **32** (27), 12; *J. Inst. Pet. Tech.*, 1934, **20**, 245A.

[220] Long residuum is a term employed to designate the residual oils from paraffinic crudes. See V. A. Kalichevsky and B. A. Stagner, "Chemical Refining of Petroleum," The Chemical Catalog Co., Inc., New York **1933**.

[221] J. R. Keith and L. C. Roess. Paper presented before the A.C.S. at Pittsburgh on Sept. 7-11, 1936.

[222] B. J. Mair and C. B. Willingham. Paper presented before Petroleum Division of the A.C.S. at Pittsburgh on Sept. 7-11, 1936. *Ind. Eng. Chem.*, 1936, **28**, 1452; *Chem. Abs.*, 1937, **31**, 1188. *J. Research Natl. Bur. Standards*, Research Paper 954, 1936, **17**, 923.

[223] A. E. Dunstan and F. B. Thole. *J. Inst. Pet. Tech.*, 1918, **4**, 191; *Chem. Abs.*, 1918, **12**, 1596; 1919, **13**, 513; *J.S.C.I.*, 1918, **37**, 291A.

[224] W. R. Wiggins, *J. Inst. Pet. Tech.*, 1936, **22**, 305; *J. Inst. Pet. Tech.*, 1936, **22**, 297A; *Chem. Abs.*, 1936, **30**, 5400.

A large number of synthetic alkyl derivatives of benzene, naphthalene and biphenyl have been studied from this viewpoint by Mikeska,[225] some of whose conclusions may be briefly summarized as follows. For hydrocarbons of a given molecular weight, the greater the complexity of the ring system, the higher is the viscosity. A long paraffinic side chain increases the viscosity index of a given hydrocarbon to a greater degree than several shorter side chains of the same total number of carbon atoms. Straight side chains are more potent in increasing the viscosity index than are branched chains. The viscosity index of a given aromatic or naphthenic hydrocarbon increases as the ratio of paraffinic to naphthenic or hydroaromatic carbon atoms is increased, provided the number of side chains remains unchanged.

PARAFFIN WAX

This substance is obtained on a large scale by refrigeration of wax-bearing distillates (admixed with a diluent) followed by filtration.[226] The slack wax so obtained is then subjected to a sweating (or partially liquefying) operation, whereby entrained oil is removed. The unmelted residuum is designated crude scale wax. The latter probably consists mainly of paraffin hydrocarbons. For example, a series of paraffins isolated by Sakhanov, Zherdeva and Vasil'ev[227] from Grozny paraffin-base crude oil had melting points varying from 28.3°C. to 71.3°C. and elementary compositions corresponding to $C_{19}H_{40}$ and $C_{35}H_{72}$ respectively. Nametkin and Nifontova[228] examined a German brown-coal paraffin and found it to have an average composition of $C_{26}H_{54}$. They report the specimen contained no more than 10 per cent of isoparaffins possessing the formula $C_{22}H_{46}$.

A white paraffin wax obtained from Pechelbronn by fractionation in a cathode vacuum was found by Yannaquis[229] to crystallize in two distinct modifications: a triclinic form appearing as separate crystals or as a network, and a monoclinic form separating as fibrous needles. From X-ray diffraction observations, Yannaquis concluded that the needle-like variety consists of open-chain paraffins with short branches and the triclinic form is probably composed of saturated cyclic hydrocarbons with long chains.[230] The presence of naphthenic hydrocarbons in refined solid paraffins is confirmed by the work of Müller and Pilat.[231] They determined carbon-hydrogen ratios corresponding to C_nH_{2n+1}, C_nH_{2n}, C_nH_{2n-2} and C_nH_{2n-3} in waxes melting at 76°C., 63°C., 57°C. and 50°C. respectively. A cyclic constitution for the fractions with a smaller hydrogen content was also indicated by the steeper slopes of their temperature-viscosity curves.[232]

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[225] L. A. Mikeska, *Ind. Eng. Chem.*, 1936, **28**, 970; *Chem. Abs.*, 1936, **30**, 6178; *J. Inst. Pet. Tech.*, 1936, **22**, 454A. See also Chapter 50.

[226] The effect of various precipitating conditions on the structure of wax separated from the propane solutions of waxy Mid-Continent long residuum has been determined to establish optimum filtration rates (A. P. Anderson and S. K. Talley, Paper presented before the Petroleum Division of the A.C.S. in Pittsburgh on Sept. 7-11, 1936).

[227] A. N. Sakhanov, L. E. Zherdeva and A. N. Vasil'ev, *Nat. Pet. News*, 1931, **23** (17), 67; *Chem. Abs.*, 1932, **26**, 586.

[228] S. S. Nametkin and S. S. Nifontova, *J. Applied Chem. (U.S.S.R.)*, 1936, **9**, 462; *Brit. Chem. Abs.* **B**, 1936, 627; *Chem. Abs.*, 1936, **30**, 7818.

[229] Yannaquis, *Ann. combustible liquides*, 1934, **9**, 295; *J. Inst. Pet. Tech.*, 1934, **20**, 451A; *Chem. Abs.*, 1934, **28**, 6288.

[230] A number of high molecular-weight isoparaffins have been synthesized by H. Guida and R. Planckh, *Ber.*, 1933, **66B**, 1445; *Chem. Abs.*, 1934, **28**, 463; *Brit. Chem. Abs.* **A**, 1933, 1270.

[231] J. Müller and S. Pilat, *Nature*, 1934, **134**, 459; *J. Inst. Pet. Tech.*, 1934, **20**, 569A; *Chem. Abs.*, 1934, **28**, 7506; *Brit. Chem. Abs.* **B**, 1934, 996.

[232] A. Berne-Allen, Jr. (Dissertation submitted to the Faculty of Pure Science of Columbia University, 1936) *made an extensive study of the solubility of refined paraffin waxes in petroleum fractions.* J. W. Poole and T. A. Mangelsdorf (*Ind. Eng. Chem.*, 1932, **24**, 1215; *Chem. Abs.*, 1933, **27**, 405; *Brit. Chem. Abs.* **B**, 1933, 7) determined the solubilities of oil and waxes in organic solvents. Specific refraction of commercial waxes in the liquid and solid states has been measured by J. M. Page, Jr. (*Ind. Eng. Chem.*, 1936, **28**, 586; *Chem. Abs.*, 1936, **30**, 6176; *J. Inst. Pet. Tech.*, 1936, **22**, 408A).

Opinions are rather divergent regarding the nature of the crystalline formations in wax, both needles and plates having been observed.[233] It is generally agreed, however, that good crystallization is inhibited by the presence of certain impurities which coat the small crystals and prevent their further growth. According to Fussteig,[234] the so-called amorphous paraffins are small crystals coated with other substances, possibly of an asphaltic nature. Treatment with an alcoholic phenol solution is said to remove the coating and permit formation of needle-shaped crystals, which can then be readily filtered. Sakhanov, Zherdeva and Vasil'ev[235] have shown that addition of even small amounts of ceresins to paraffin wax greatly modifies the crystalline structure as well as its filtering and sweating properties. An X-ray study of recrystallized fractions of paraffins from Fushun shale oil has been made by Sakurada, Fuchino, Tsuneoka and Matsushita[236] who concluded that these materials consisted exclusively of normal paraffins.[237]

The solid hydrocarbons called ceresins display both chemical and physical properties quite different from paraffin wax. In contrast to paraffins, ceresins retain oil very tenaciously and cannot be separated therefrom by the usual process of filtering and pressing. At similar melting points, the ceresins have a much higher molecular weight, specific gravity, viscosity, boiling point and nitrobenzene points than the paraffins. They have a very delicate crystalline structure, the crystals being of needle or short plate shape. Chemically the ceresins are much less stable than solid paraffins and react readily with fuming sulphuric or with chlorosulphonic acid, a fact which has been interpreted to indicate an isoparaffinic structure. On account of their high boiling point, they can be partially separated from paraffin wax. Sakhanov and his collaborators[238] have demonstrated that ceresins can be distilled without decomposition under high vacua but at high pressures they undergo partial transformation to paraffin waxes. A series of ceresins isolated by these investigators from Surakhany crude oils had elementary compositions and molecular weights corresponding to the formulas $C_{37}H_{76}$ to $C_{53}H_{108}$. It was concluded that the latter compounds form a part of the paraffin series and are probably branched chain in structure.

Müller and Pilat[239] report that a specimen of ceresin (from a Boryslaw petroleum) gave fractions having a hydrogen content lower than that required for a paraffin hydrocarbon. Other physical characteristics of these fractions supported a cyclic structure. Another sample, secured during separation of asphalts and resins (from Boryslaw crude oil) with methane at low temperatures followed by repeated precipitation of the ceresin from solvents, appeared to contain both cyclic and paraffinic hydrocarbons. On the other hand, the relatively low refractive indices and specific gravities of the products suggest the presence of large polymethylenic rings, which might be considered as double chains. Also, it has been stated that a wax secured from Midcontinent petroleum contained a portion which melted about 30°C. lower than the corresponding normal paraffins.[239a] This low-melting fraction was said to consist chiefly of cyclic hydrocarbons.

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[233] F. H. Rhodes, C. W. Mason and W. R. Sutton, *Ind. Eng. Chem.*, 1927, **19**, 935; *Chem. Abs.*, 1927, **21**, 3125; *Brit. Chem. Abs.* **B**, 1927, 739. G. D. Graves, *Ind. Eng. Chem.*, 1931, **23**, 762; *Chem. Abs.*, 1931, **25**, 4694; *Brit. Chem. Abs.* **B**, 1931, 1002. S. W. Ferris, H. C. Cowles, Jr., and L. M. Henderson, *Ind. Eng. Chem.*, 1931, **23**, 681; *Chem. Abs.*, 1931, **25**, 3816; *Brit. Chem. Abs.* **B**, 1931, 708.

[234] R. Fussteig, *Petroleum Z.*, 1935, **31** (7), 1; *Chem. Abs.*, 1935, **29**, 6746.

[235] A. N. Sakhanov, L. E. Zherdeva and A. N. Vasil'ev, *Nat. Pet. News*, 1931, **23** (19), 71; *Chem. Abs.*, 1931, **25**, 5008.

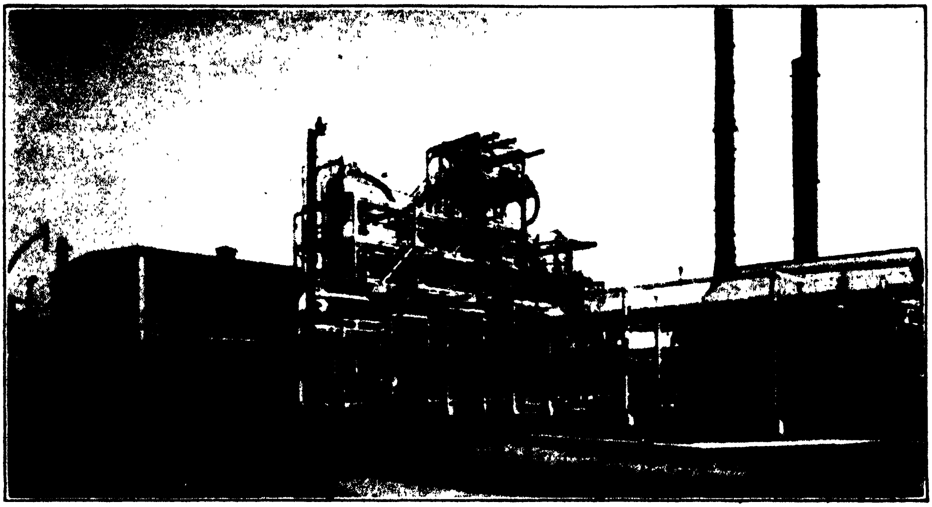
[236] I. Sakurada, K. Fuchino, S. Tsuneoka and Y. Matsushita, *J. Soc. Chem. Ind., Japan*, 1935, **38**, Suppl. Bind., *670*, *671*, *674* and *677*; *Brit. Chem. Abs.* **B**, 1936, 178; *Chem. Abs.*, 1936, **30**, 2738.

[237] Industrial methods for the production and refining of paraffin wax from petroleum are described by R. H. Espach, *Bur. Mines, Bull.*, 1935, 388; *J. Inst. Pet. Tech.*, 1936, **22**, 359A; *Chem. Abs.*, 1936, **30**, 4305; *Brit. Chem. Abs.* **B**, 1936, 403. See also O. Brück, *Rev. Petrolifere*, **1934**, 377; *J. Inst. Pet. Tech.*, 1934, **20**, 360A; *Chem. Abs.*, 1934, **28**, 4885.

[238] A. N. Sakhanov, L. E. Zherdeva and A. N. Vasil'ev, *Nat. Pet. News*, 1931, **23** (16), 49; **23** (17), 67; **23** (18), 51; **23** (19), 71; *Chem. Abs.*, 1931, **25**, 5008.

[239] J. Müller and S. Pilat, *J. Inst. Pet. Tech.*, 1935, **21**, 887; *Chem. Abs.*, 1936, **30**, 2355; *J. Inst. Pet. Tech.*, 1935, **21**, 451A; *Brit. Chem. Abs.* **B**, 1936, 51.

By fractional extraction of "Vaseline" with acetone, André and Bloch[240] effected its separation into three main fractions of decreasing solubility, namely (1) a fraction of low optical activity, having a composition corresponding to $C_{19}H_{38}$ and probably cyclic, (2) a middle fraction with high density and rotation, from which a hydrocarbon, $C_{28}H_{52}$, possibly related to cholestane, was isolated, and (3) the least soluble portion with the composition $C_{30}H_{70}$, probably a mixture of highly condensed cyclic and aliphatic hydrocarbons.



Courtesy Standard Oil Co. of Louisiana

FIG. 6.—Plant for Phenol Extraction of Lubricating Oils.

Wenzel and Weiser[241] examined a Hodonin petroleum and found the presence apparently of a saturated hydrocarbon of the formula $C_{28}H_{46}$. Upon further analysis this hydrocarbon was shown to contain 1 benzene ring and 2 naphthene rings. $C_{15}H_{30}$, a monocyclic naphthene hydrocarbon and $C_{15}H_{28}$, $C_{17}H_{32}$, $C_{18}H_{34}$, $C_{19}H_{36}$ and $C_{20}H_{38}$, all bicyclic naphthenes, were found in the high-boiling fractions of Ni-itsu (Japanese) crude oil.[242] Gruse[243] indicates that $C_{60}H_{122}$ is the largest hydrocarbon isolated from paraffin wax. Low-temperature tar and some of its cracked distillates have been found to contain anthracene, 2-methyl-, 2,6-dimethyl, 2,3,6-trimethyl- and 2,3,6,7-tetramethyl-anthracene.[244]

[239a] B. J. Mair and S. T. Schicktanz, *Ind. Eng. Chem.*, 1936, **28**, 1056; *J. Inst. Pet. Tech.*, 1936, **22**, 458A; *Chem. Abs.*, 1936, **30**, 7831; *Brit. Chem. Abs.* B, 1936, 1077.

[240] E. André and A. Bloch, *Bull. soc. chim.*, 1935, **2**, 802; *Brit. Chem. Abs.* B, 1935, 710.

[241] F. Wenzel and H. Weiser, *J. prakt. Chem.*, 1936, **144**, 145; *Chem. Abs.*, 1936, **30**, 4655.

[242] R. Kobayashi, *J. Soc. Chem. Ind., Japan*, 1936, **39**, Suppl. Bind., 142; *Chem. Abs.*, 1936, **30**, 5399; *Brit. Chem. Abs.* B, 1936, 626.

[243] W. A. Gruse, "Petroleum and its Products," McGraw-Hill Book Company, Inc., New York, 1928, page 16. A. Gascard (*Ann. Chim.*, 1921, **15**, 332; *Chem. Abs.*, 1922, **16**, 48; *J.C.S.*, 1921, **120** (1), 536) reported the synthesis of tetrahexacontane, $C_{64}H_{130}$, probably the largest petroleum hydrocarbon molecule.

[244] G. T. Morgan and E. A. Coulson, *J.S.C.I.*, 1934, **53**, 71T; *Chem. Abs.*, 1934, **28**, 3221; *Brit. Chem. Abs.* B, 1934, 312; *J. Inst. Pet. Tech.*, 1934, **20**, 317A. It has been shown that a mixture of monomethyl naphthalene isomers are found in low-temperature tars. (G. T. Morgan and E. A. Coulson,

One application of high-molecular-weight, amorphous, waxy bodies, e.g., petrolatum, is for the spraying of coal or coke to reduce dusting of the latter during handling.[244a] The hydrocarbon material, which is too viscous to flow readily at ordinary temperatures, is heated until it becomes fluid and then applied to the solid fuel in the form of a fine mist. Another procedure comprises dipping coal into an aqueous suspension of paraffin wax.[244b] Asphaltic oils, of 19° to 30° Bé. at 15°C., have also been proposed.[244c]

SOLVENT EXTRACTION

The discovery that certain solvents can be employed to effect a partial segregation of petroleum distillates, particularly lubricating oil fractions, into two fractions of widely different characteristics has resulted in the industrial development of refining processes based on this principle.[245] The main purpose of the solvent treatment of lubricating oils is improvement in viscosity index although an improvement in color, Conradson carbon and resistance to oxidation is simultaneously obtained. The lubricating oil is treated with a solvent or mixture of solvents, usually in a continuous countercurrent system, with the result that undesirable hydrocarbon types (usually referred to as naphthenic oils but probably consisting of cyclic hydrocarbons of several types, including aromatics) are dissolved and the raffinate becomes more paraffinic and exhibits improved viscosity-temperature characteristics. The original oil is thus split up into two main fractions: (1) the insoluble paraffinic portion having enhanced lubricant properties and (2) the soluble portion containing hydrocarbons of inferior properties from the viewpoint of lubrication.

The suitability of any particular solvent for the improvement of lubricating oils depends not only on its selective action but also on its cost, availability, ease of recovery, stability and inertness. Of the many solvents suggested or claimed for this purpose, a number of the following have attained the stage of industrial application.

Nitrobenzene[246] which has a high solvent power so that relatively low temperatures are used.

A mixture of liquid sulphur dioxide and benzene[247] is reported to possess

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J.S.C.I., 1934, **53**, 73T; *Chem. Abs.*, 1934, **28**, 3402; *J. Inst. Pet. Tech.*, 1934, **20**, 241A; *Brit. Chem. Abs.* B, 1934, 312).

[244a] Carleton Ellis, U. S. P. 2,076,497, Apr. 6, 1937, to Standard Oil Development Co.; *Chem. Abs.*, 1937, **31**, 3671.

[244b] H. R. Fife, U. S. P. 1,912,697, June 6, 1933; *Chem. Abs.*, 1933, **27**, 4379; *Brit. Chem. Abs.* B, 1934, 229.

[244c] A. O. Vinz, U. S. P. 2,005,512, June 18, 1935; *Chem. Abs.*, 1935, **29**, 5253; *Brit. Chem. Abs.* B, 1936, 356.

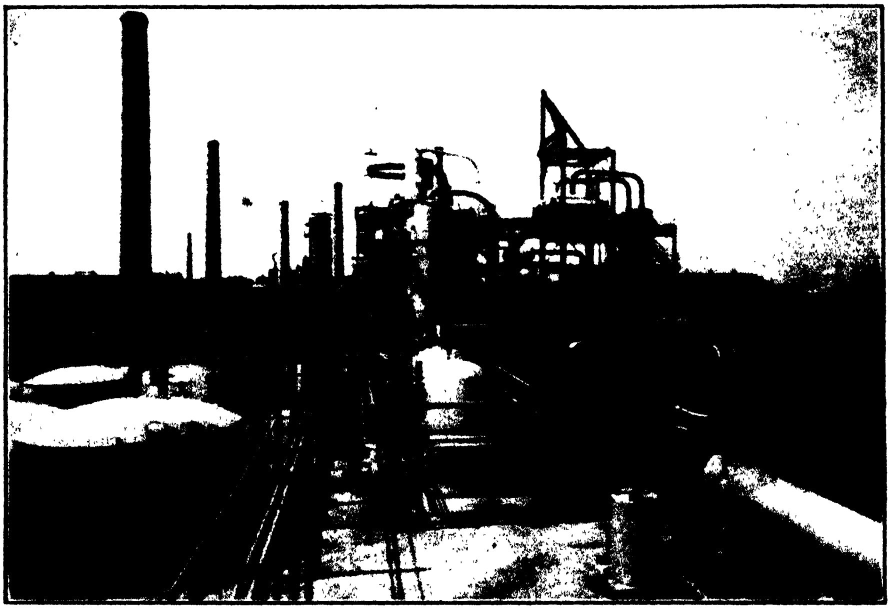
[245] Reviews on solvent refining have been contributed by W. T. Ziegenhain (*Oil & Gas J.*, 1934, **32** (45), 44; *J. Inst. Pet. Tech.*, 1934, **20**, 324A), J. T. Ward and H. O. Forrest (*Chem. Met. Eng.*, 1935, **42**, 246; *Brit. Chem. Abs.* B, 1935, 615; *Chem. Abs.*, 1935, **29**, 4925). E. H. J. Rosenberg (*Proc. World Petroleum Congr.*, 1933, **2**, 338; *J. Inst. Pet. Tech.*, 1934, **20**, 322A; *Chem. Abs.*, 1934, **28**, 4874; *Brit. Chem. Abs.* B, 1934, 787), K. Fürst (*Petroleum Z.*, 1933, **29**, No. 44; *Motorenbetrieb und Maschinen-Schmierung*, 1933, **6** (11), 2; *Chem. Abs.*, 1934, **28**, 3881; *Brit. Chem. Abs.* B, 1934, 51), C. G. Verver and R. N. J. Saal (*J. Inst. Pet. Tech.*, 1934, **20**, 367; *Chem. Abs.*, 1934, **28**, 4581; *J. Inst. Pet. Tech.*, 1934, **20**, 414A) and W. R. Wiggins and F. C. Hall (*J. Inst. Pet. Tech.*, 1936, **22**, 78; *Brit. Chem. Abs.* B, 1936, 308; *Chem. Abs.*, 1936, **30**, 2357; *J. Inst. Pet. Tech.*, 1936, **22**, 160A). R. E. Wilson and P. C. Keith, Jr. (*Refiner*, 1934, **13**, 252; *J. Inst. Pet. Tech.*, 1934, **20**, 528A; *Chem. Abs.*, 1934, **28**, 6291) have discussed the economic aspects of solvent extraction processes.

[246] S. W. Ferris and W. F. Houghton, *Refiner*, 1933, **12**, 328; *Chem. Abs.*, 1933, **27**, 5526. S. W. Ferris and W. F. Houghton, *Proc. World Petroleum Congr.*, 1933, **2**, 370; *J. Inst. Pet. Tech.*, 1934, **20**, 323A; *Chem. Abs.*, 1934, **28**, 4874. S. W. Ferris, W. A. Myers and A. G. Peterkin, *Refiner*, 1933, **12**, 435; *J. Inst. Pet. Tech.*, 1934, **20**, 32A; *Chem. Abs.*, 1934, **28**, 1174. S. W. Ferris, *J. Franklin Inst.*, 1934, **217**, 591; *Chem. Abs.*, 1934, **28**, 5642; *Brit. Chem. Abs.* B, 1934, 563; U. S. P. 1,941,601, Jan. 2, 1934, to Atlantic Refining Co., *J. Inst. Pet. Tech.*, 1934, **20**, 191A; *Brit. Chem. Abs.* B, 1934, 791. Y. A. Pinkevich, *Neft. Khoz.*, 1935, **29** (11), 58; *J. Inst. Pet. Tech.*, 1937, **23**, 29A.

[247] J. A. Buchel and R. N. J. Saal, U. S. P. 1,945,516, Feb. 6, 1934, to Shell Development Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 334A; *Chem. Abs.*, 1934, **28**, 2517. W. Grote, H. Krekeler and H.

greater solvent power than sulphur dioxide. Various modifications of solvent extraction with sulphur dioxide alone, or in admixture with other solvents have been suggested.[248]

Phenol has been employed on a technical scale for several years.[249] Suggested modifications include the use of this compound admixed with 5-35 per cent of methanol,[250] a mixture of liquid ethane and propane[251] or diluted with cyclohexanol.[252] According to Kuczynski,[253] phenol cannot be used successfully with



Courtesy Max B. Miller & Co., Inc.

FIG. 7.—Solvent Extraction Plant Employing Duo-Sol Process.

Ramser, *Proc. World Petroleum Congr.*, 1933, 2, 359; *Chem. Abs.*, 1934, **28**, 4874 L. P. Stockman, *Oil & Gas J.*, 1934, **33** (13), 6; *J. Inst. Pet. Tech.*, 1934, **20**, 615A. O. P. Cottrell, *Refiner*, 1933, **12**, 432; *J. Inst. Pet. Tech.*, 1934, **20**, 34A; *Chem. Abs.*, 1934, **28**, 1176. R. S. Fussteig, *Petroleum Eng.*, 1936, 7 (13), 36; *J. Inst. Pet. Tech.*, 1936, **22**, 548A.

[248] British P. 398,992, and 399,030, 1932, to Edeleanu G.m.b.H.; *Brit. Chem. Abs.* **B**, 1933, 1045. W. Grote and P. Obergfell, U. S. P. 1,945,500, Jan. 30, 1934, to Edeleanu G.m.b.H.; *Brit. Chem. Abs.* **B**, 1934, 919; *Chem. Abs.*, 1934, **28**, 2520; *J. Inst. Pet. Tech.*, 1934, **20**, 192A. J. T. Rutherford, U. S. P. 2,024,476, Dec. 17, 1935, to Standard Oil Co. of California; *Chem. Abs.*, 1936, **30**, 1219. U. B. Bray and C. E. Swift, Canadian P. 344,453, 1934, to Union Oil Co. of California; *Chem. Abs.*, 1935, **29**, 2346. F. B. Thole and S. F. Birch, British P. 433,197, 1934, to Anglo-Iranian Oil Co., Ltd.; *Brit. Chem. Abs.* **B**, 1935, 937. A. Lazar, *Ind. Eng. Chem.*, 1936, **28**, 658; *J. Inst. Pet. Tech.*, 1936, **22**, 368A; *Chem. Abs.*, 1936, **30**, 5433; *Brit. Chem. Abs.* **B**, 1936, 800. G. M. Woods, *Petroleum Eng.*, 1936, 7 (9), 107; *J. Inst. Pet. Tech.*, 1936, **22**, 364A. R. T. Leslie (*J. Research Nat. Bur. Standards*, 1934, **13**, 589; *Chem. Abs.*, 1935, **29**, 987) has determined the critical solution temperatures of paraffin and naphthene hydrocarbons of the naphtha fraction of petroleum in sulphur dioxide.

[249] R. K. Stratford, O. S. Pokorny and J. L. Huggett, *Refiner*, 1933, **12**, 458; *J. Inst. Pet. Tech.*, 1934, **20**, 33A; *Chem. Abs.*, 1934, **28**, 1176. R. K. Stratford, H. H. Moor and O. S. Pokorny, *Proc. World Petroleum Congr.*, 1933, 2, 362; *Brit. Chem. Abs.* **B**, 1934, 949; *J. Inst. Pet. Tech.*, 1934, **20**, 184A; *Chem. Abs.*, 1934, **28**, 4874.

[250] R. K. Stratford, Canadian P. 334,377, 1933, to Standard Oil Development Co.; *Chem. Abs.*, 1933, **27**, 5530.

[251] J. M. Whiteley, Jr., U. S. P. 2,025,965, Dec. 31, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 1221; *Brit. Chem. Abs.* **B**, 1936, 820. The solubility of dotriacontane in propane and butane has been investigated by W. F. Seyer and R. Fordyce, *J.A.C.S.*, 1936, **58**, 2029.

[252] D. F. Edwards and J. V. Starr, Canadian P. 338,558, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1934, **28**, 2174.

oils containing very high proportions of aromatic hydrocarbons. As a substitute, cresol has been proposed either alone[254] or in conjunction with other solvents.[255] In particular, a mixture of cresol and propane is employed in the "Duo-Sol" process,[256] this combination having specific solvent powers for the unsaturated and cyclic constituents (in cresol) and for the saturated components (in the hydrocarbon). (See Fig. 7.) Since the two solvents are immiscible with each other, an effective separation of the two portions mentioned is said to be accomplished, with a relatively low loss of solvent. The process is reported to be applicable in the preparation of lubricating oils from heavy stocks, both residuals and distillates. A combination of liquefied hydrocarbon gases (ethane or propane) and phenol is suggested for the same purpose.[257]

One advantage of Chlorex (β,β'-dichloroethyl ether) in solvent refining is its high specific gravity which promotes rapid separation of the raffinate and the extract layers.[258] A mixture of this compound with liquid sulphur dioxide with or without liquefied, normally gaseous hydrocarbons, such as propane, is also proposed.[259]

Another solvent-refining agent is furfural.[260] In this instance extraction is usually effected at about 200°F. though a temperature gradient is often employed in countercurrent operations. Aromatic constituents may be removed from naphthas by the use of this liquid.[261]

Crotonaldehyde and acrolein have been recommended for the solvent extraction of lubricating oils.[262] The contact temperature in the case of crotonaldehyde is said to be 60°F.-70°F.

Other organic solvents which have been advanced for the selective removal of hydrocarbons and undesirable non-hydrocarbons from lubricating stocks include

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[253] T. Kuczyński, *Petroleum Z.*, 1934, **30** (3), 9; *Chem. Abs.*, 1934, **28**, 3878; *Brit. Chem. Abs.* **B**, 1934, 308.

[254] H. Suida and H. Poll, *Petroleum Z.*, 1934, **30** (25), 4; *Brit. Chem. Abs.* **B**, 1934, 787; *Chem. Abs.*, 1935, **29**, 1235. H. Burstin, *Przemysl Chem.*, 1934, **18**, 341; *J. Inst. Pet. Tech.*, 1935, **21**, 133A; *Chem. Abs.*, 1935, **29**, 6412, *Brit. Chem. Abs.* **B**, 1935, 133.

[255] L. A. Clarke, U. S. P. 1,974,805, Sept. 25, 1934, to Texas Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 583A; *Brit. Chem. Abs.* **B**, 1935, 713; *Chem. Abs.*, 1934, **28**, 7516. H. Suida, H. Poll and A. Nowak, British P. 436,194, 1935; *Brit. Chem. Abs.* **B**, 1935, 1127; *J. Inst. Pet. Tech.*, 1935, **21**, 459A.

[256] M. B. Miller, *Refiner*, 1933, **12**, 453; *Oil & Gas J.*, 1934, **32** (21), 11; *Nat. Pet. News*, 1933, **25** (41), 26; *Chem. Abs.*, 1934, **28**, 305. J. V. Hightower, *Chem. Met. Eng.*, 1935, **42**, 82; *Brit. Chem. Abs.* **B**, 1935, 536; *Chem. Abs.*, 1935, **29**, 3503; *J. Inst. Pet. Tech.*, 1935, **21**, 133A.

[257] British P. 421,123, 1934, to M. B. Miller & Co.; *Chem. Abs.*, 1935, **29**, 3820; *Brit. Chem. Abs.* **B**, 1935, 136; *J. Inst. Pet. Tech.*, 1935, **21**, 100A. M. H. Tuttle, British P. 424,000, 1935, to M. B. Miller & Co.; *J. Inst. Pet. Tech.*, 1935, **21**, 175A; *Brit. Chem. Abs.* **B**, 1935, 346; *Chem. Abs.*, 1935, **29**, 4571.

[258] A. L. Foster, *Nat. Pet. News*, 1933, **25** (33), 35. J. M. Page, C. C. Buchler and S. H. Diggs, *Nat. Pet. News*, 1933, **25** (14), 35; *J. Inst. Pet. Tech.*, 1933, **19**, 190A. W. H. Bahlke, A. B. Brown and F. F. Diwoky, *Refiner*, 1933, **12**, 445; *Oil & Gas J.*, 1933, **32** (23), 60; *Chem. Abs.*, 1934, **28**, 302; *J. Inst. Pet. Tech.*, 1934, **20**, 31A. U. B. Bray, R. C. Pollock and D. R. Merrill, *Proc. Am. Petroleum Inst., 5th Mid-Year Meeting, Sect. III*, 1936, **16**, 135; *Oil & Gas J.*, 1935, **34** (2), 18; *Refiner*, 1935, **14**, 307; *Chem. Abs.*, 1937, **31**, 530.

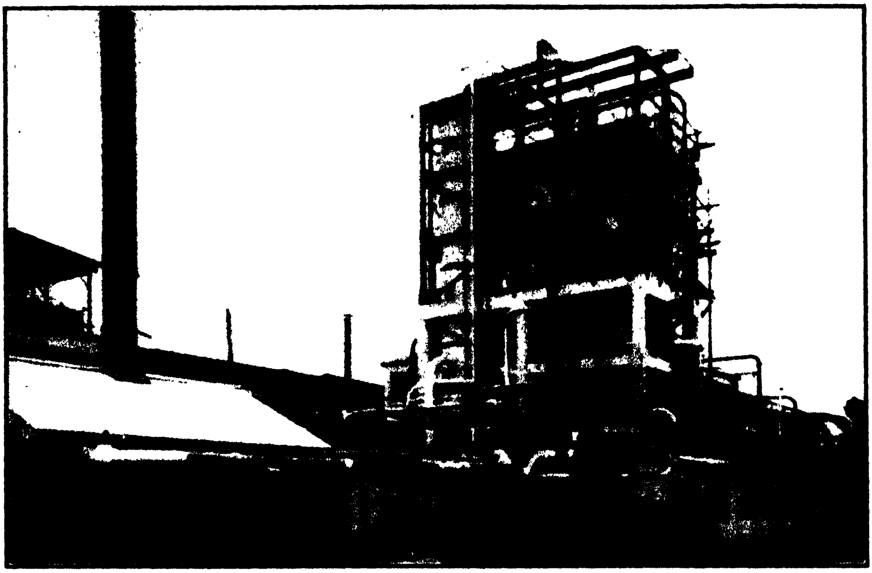
[259] D. R. Merrill and P. Sulkow, U. S. P. 1,948,042, Feb. 20, 1934, to Union Oil Co. of California; *Brit. Chem. Abs.* **B**, 1934, 1048; *Chem. Abs.*, 1934, **28**, 2892; *J. Inst. Pet. Tech.*, 1934, **20**, 334A.

[260] E. Eichwald, U. S. P. 1,550,523, June 2, 1923, to Bataafsche Petroleum Maatschappij; *J.S.C.I.*, 1925, **44**, 837B; *Chem. Abs.*, 1926, **20**, 108. R. E. Manley, B. Y. McCarty and H. H. Gross, *Refiner*, 1933, **12**, 420; *Nat. Pet. News*, 1933, **25** (43), 26; *J. Inst. Pet. Tech.*, 1934, **20**, 33A; *Oil & Gas J.*, 1933, **32** (23), 78, 79, 81, 82; *Chem. Abs.*, 1934, **28**, 302. H. H. Gross, U. S. P. 1,962,103, June 5, 1934, to Texas Co.; *Brit. Chem. Abs.* **B**, 1935, 295; *Chem. Abs.*, 1934, **28**, 4897; *J. Inst. Pet. Tech.*, 1934, **20**, 504A. R. E. Manley and H. H. Gross, U. S. P. 1,971,753, Aug. 28, 1934, to Texas Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 541A; *Brit. Chem. Abs.* **B**, 1935, 713; *Chem. Abs.*, 1934, **28**, 6560. R. E. Manley, U. S. P. 2,000,707, May 7, 1935, to Texas Co.; *Chem. Abs.*, 1935, **29**, 4164; *J. Inst. Pet. Tech.*, 1935, **21**, 268A. U. S. P. 2,054,433, Sept. 15, 1936; *Chem. Abs.*, 1936, **30**, 7840; *J. Inst. Pet. Tech.*, 1936, **22**, 549A. F. X. Govers, U. S. P. 2,054,052, Sept. 8, 1936, to Indian Refining Co.; *Chem. Abs.*, 1936, **30**, 7840; *J. Inst. Pet. Tech.*, 1936, **22**, 549A. British P. 454,690, 1936, to Texaco Development Corp.; *J. Inst. Pet. Tech.*, 1937, **23**, 30A; *Chem. Abs.*, 1937, **31**, 1603.

[261] W. M. Stratford, Canadian P. 348,523, 1935, to Texaco Development Corp.; *Chem. Abs.*, 1935, **29**, 3508.

[262] J. W. Poole and J. M. Wadsworth, *Refiner*, 1933, **12**, 412; *J. Inst. Pet. Tech.*, 1934, **20**, 31A J. W. Poole, U. S. P. 1,965,392, July 3, 1934; *J. Inst. Pet. Tech.*, 1934, **20**, 540A; *Brit. Chem. Abs.* **B**, 1935, 346; *Chem. Abs.*, 1934, **28**, 5655.

furfuryl alcohol,[263] furfuraldoxime,[264] tetrahydrofurfuryl alcohol,[265] tetrahydrofurfuran,[266] benzoyl,- toluyl- or xyloylfurans,[267] ethylene glycol monoacetate,[268] ethyl lactate,[268a] liquid trimethylene,[269] benzaldehyde,[270] propionaldehyde,[271] methyl acetate,[272] aliphatic or aromatic thiocyanates or isothiocyanates,[273] ketones,[274] propionitrile[275] and a mixed aliphatic-aromatic amine as phenylmethylamine.[276]



Courtesy Standard Oil Development Co.

FIG. 8.—Phenol-extraction Plant.

The relationship between aromaticity of lubricating oils and other oil properties has been discussed by von Fuchs and Anderson,[277] particularly in connection with the measurement of the improvement attainable on solvent extraction.

[263] J. B. Hill, Canadian P. 334,463, 1933, to Atlantic Refining Co.; *Chem. Abs.*, 1933, **27**, 5530.

[264] M. T. Kendall, U. S. P. 1,973,683, Sept. 11, 1934, to Texas Co.; *Brit. Chem. Abs.* B, 1935, 712; *Chem. Abs.*, 1934, **28**, 6994.

[265] J. G. Detwiler, Canadian P. 347,767, 1935, to Texaco Development Corp.; *Chem. Abs.*, 1935, **29**, 3148.

[266] E. F. Pevere, U. S. P. 1,998,399, Apr. 16, 1935, to Texas Co.; *Chem. Abs.*, 1935, **29**, 3820.

[267] L. A. Clarke, U. S. P. 2,000,690, May 7, 1935, to Texas Co.; *Chem. Abs.*, 1935, **29**, 4164.

[268] K. B. Edwards and R. Lacey, *J.S.C.I.*, 1935, **54**, 253T; *Chem. Abs.*, 1935, **29**, 6746; *Brit. Chem. Abs.* B, 1935, 836; *J. Inst. Pet. Tech.*, 1935, **21**, 341A.

[268a] French P. 798,304, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 7320.

[269] W. M. Stratford, U. S. P. 1,962,622, June 12, 1934, to Texas Co.; *Chem. Abs.*, 1934, **28**, 4898; *Brit. Chem. Abs.* B, 1935, 346.

[270] F. X. Govers, U. S. P. 1,995,147, Mar. 19, 1935, to Indian Refining Co.; *Chem. Abs.*, 1935, **29**, 3150.

[271] E. R. Birkhimer, Canadian P. 335,392, 1933, to Atlantic Refining Co.; *Chem. Abs.*, 1933, **27**, 5529.

[272] L. A. Clarke, Canadian P. 342,294, 1934, to Texaco Development Corp.; *Chem. Abs.*, 1934, **28**, 5658.

[273] S. W. Ferris, Canadian P. 335,135, 1933, to Atlantic Refining Co.; *Chem. Abs.*, 1933, **27**, 5530.

[274] British P. 413,307, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 594; French P. 748,925, 1933; *Chem. Abs.*, 1934, **28**, 313. F. F. Diwoky and A. B. Brown, Canadian P. 346,406, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 2347.

[275] H. F. Lindeke and B. S. Greensfelder, British P. 444,535, 1935, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* B, 1936, 486; *Chem. Abs.*, 1936, **30**, 6547.

[276] L. M. Henderson, U. S. P. 2,024,221, Dec. 17, 1935, to Atlantic Refining Company; *Chem. Abs.*, 1936, **30**, 1224; *Brit. Chem. Abs.*, B, 1936, 821.

[277] G. H. von Fuchs and A. P. Anderson, paper presented before the Petroleum Division of the A.C.S. in Pittsburgh on Sept. 7-11, 1936.

It has been found that a partial segregation of the constituents of lubricating oils can be accomplished by saturating a solution of such oils in liquefied gases, such as propane, with natural gas under pressure. Early work along these lines is given by Todo.[278] He obtained a product nearly equal to gasoline as a fuel by saturating hydrocarbons obtained by distillation of petroleum with artificial or natural gas under high pressure and at a low temperature. Neyman and Pilat[279] have shown that the thermal effects of dissolving natural gas in hydrocarbons are practically restricted to the heat of compression. Manley[280] has proposed a method of precipitating wax from a hydrocarbon oil chilled to —18°C. by direct vaporization from it of a liquefied normally gaseous diluent, such as propane, in the presence of an inert solid material.

By increasing the pressure of the natural gas (mostly methane) up to 130 atmospheres petroleum residues dissolved in liquid propane can be separated at room temperature into a series of fractions of decreasing density and viscosity.[281]

Table 8 gives some results obtained by Pilat on the fractionation with natural gas of a Rumanian petroleum residue dissolved in liquid propane.

TABLE 8.—*Fractionation of a Rumanian Petroleum Residue.*

Press. in Atmos.	Ppt. in Gals.	Yield %	Spec. Grav.	Viscosity (Saybolt) at 37.8°C.	Viscosity Index[a]	Pour Point °C.	Boiling Point °C.
8	805	27.35	...	...	...	...	...
30	137	4.65	0.997	...	...	...	...
40	261	8.85	0.9845	...	...	...	...
50	145	4.95	0.960	26,658	...	+ 8	
60	278	9.45	0.9495	10,366	58	+ 5.5	275
70	273	9.27	0.939	6,354	61	+ 4	277
80	206	7.00	0.9295	3,703	64	+ 9	267
90	188	6.4	0.9225	2,363	64	+ 3	263
100	128	4.35	0.9165	1,602	60	0	...
130	154	5.25	0.909	1,056	62	− 6	249
Residue	122	4.15	0.908	615	57	−13	...

[a] See Chapter 50.

"At 8 atmospheres, which is the pressure of the propane fraction used, asphalts are precipitated; methane is then charged, and at 40 atmospheres coloring substances of highly aromatic character (molecular weight only about 450 to 500 in spite of high viscosity at room temperature) are precipitated. Upon further pressure increases, oily fractions appear as a second, heavier liquid phase." These oil

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[278] P. Todo, Japanese P. 32,460, 1918; *Chem. Abs.*, 1918, **12**, 2247.

[279] E. Neyman and S. Pilat, *Oil & Gas J.*, 1935, **33** (49), 13; *Brit. Chem. Abs.* **B**, 1936, 625; *Chem. Abs.*, 1935, **29**, 6021. *Oil & Gas J.*, 1936, **35** (10), 54; *J. Inst. Pet. Tech.*, 1936, **22**, 444A.

[280] R. E. Manley, U. S. P. 2,040,056, May 5, 1936, to the Texas Co.; *Chem. Abs.*, 1936, **30**, 4313; *J. Inst. Pet. Tech.*, 1936, **22**, 318A. *Cf.* S. A. Montgomery, U. S. P. 2,053,872, Sept. 8, 1936, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1936, **30**, 7839; *J. Inst. Pet. Tech.*, 1936, **22**, 549A. Also D. B. Banks and P. D. Barton, U. S. P. 2,059,166, Oct. 27, 1936, to Sun Oil Co.; *Chem. Abs.*, 1937, **31**, 250. Canadian P. 360,668, 1936; *Chem. Abs.*, 1936, **30**, 7839.

[281] M. Godlewicz and S. V. Pilat, *Przemysl Chem.*, 1934, **18**, 376; *Brit. Chem. Abs.* **B**, 1935, 131; *Chem. Abs.*, 1935, **29**, 6408; *J. Inst. Pet. Tech.*, 1935, **21**, 60A. S. Pilat, *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 655; *Brit. Chem. Abs.* **B**, 1935, 1030; *Chem. Abs.*, 1935, **29**, 8302; *J. Inst. Pet. Tech.*, 1935, **21**, 401A; *Oil & Gas J.*, 1936, **35** (10), 54; *Chem. Abs.*, 1936, **30**, 7825; *J. Inst. Pet. Tech.*, 1936, **22**, 444A. Pilat has determined the pressure at which precipitation is effected with other gases. He used a solution consisting of 1 part of de-asphaltized Venezuelan residue to 6.1 parts of solvent (propane-butane fraction). The pressure of the gaseous precipitant required to effect the first sign of turbidity is indicated in the following table.

Gas	Pressure in atmospheres
CO_2	15
Natural Gas (97.9% methane)	18
Nitrogen	28
H_2	no turbidity up to 86 atmospheres.

fractions which separate out contain propane and small amounts of methane. Pilat remarks that very light heating easily removes the last traces of these solvents.

The use of propane (or other liquefied gases) with oils refined with chloroaniline[282] has been proposed for improving lubricating qualities. In addition to being a useful constituent of a combination of selective solvents for such oils, this hydrocarbon may be employed for the precipitation of asphaltic substances from crude oils and for the dewaxing of residual or distillate oils.[283] (For example, see Fig. 9.)

Liquefied low-boiling hydrocarbons have also been applied as extracting agents in the purification of rosin, with or without the use of an intermediate solvent, as gasoline[284] and in the removal of resins and terpenes from coniferous wood, e.g., long leaf yellow pine.[285]

INORGANIC CONSTITUENTS OF CRUDE OIL

Crude petroleum contains, in addition to water with which it frequently forms stable emulsions, considerable proportions of inorganic materials. Up to 1913, the known inorganic constituents comprised the elements silicon, arsenic, phosphorus, aluminum, iron, calcium, magnesium, copper, silver, gold, vanadium and sodium. This list has subsequently been increased by the addition of the elements titanium, lead, tin, nickel, manganese, chromium, barium, strontium, potassium and lithium. The actual form in which these elements are present is not known; but certain of them, for example, vanadium and iron, may be organically combined. The iron content may be derived from pipe lines and tanks or from ferruginous rocks, and silicates may be found in solution in small quantities owing to their saponaceous properties. In general, the composition of the petroleum ash probably bears a close relation to the class of rock with which the oil has been in contact. Thus, it is suggested that Ohio oils contain lime and magnesia as a result of solvent action on the dolomitic rocks of that region.[286]

The existence of vanadium in the ash of nearly all crude oils is of interest. Vinogradov and Bergman[287] have examined the ash, particularly uranium and vanadium contents, of petroleums and bitumens of the U.S.S.R. They report the latter element (vanadium) is present to the extent of 0.1 per cent in asphaltite[288] and 0.00001 per cent in petroleum and is proportional to the organic content and not to the ash. The theory that vanadium passes into petroleum as vanadium pentasulphide from aqueous solution in the presence of hydrogen sulphide, is considered untenable by these investigators. It is suggested that the vanadium probably came from organic material deposited in sea basins and was concentrated by marine organisms.

According to Longobardi[289] vanadium is present in organic materials including

[282] British P. 426.221, 1933, Standard Oil Co. of Ind.; *Brit. Chem. Abs.* **B**, 1935, 486.

[283] M. B. Bray, C. E. Swift and D. E. Carr, *Refiner*, 1934, **13**, 333; *J. Inst. Pet. Tech.*, 1934, **20**, 575A. R. C. Conine, *Oil & Gas J.*, 1934, **33** (31), 17; *J. Inst. Pet. Tech.*, 1935, **21**, 61A. W. H. Bahlke, R. N. Giles and C. E. Adams, *Refiner*, 1933, **12**, 229; *Chem. Abs.*, 1933, **27**, 5524.

[284] I. W. Humphrey, U. S. P. 1,806,973, May 26, 1931, to Hercules Power Co.; *Brit. Chem. Abs.* **B**, 1932, 235; *Chem. Abs.*, 1931, **25**, 4139.

[285] A. D. Little, U. S. P. 1,762,785, June 10, 1930, to A. D. Little, Inc.; *Brit. Chem. Abs.* **B**, 1931, 154; *Chem. Abs.*, 1930, **24**, 3898.

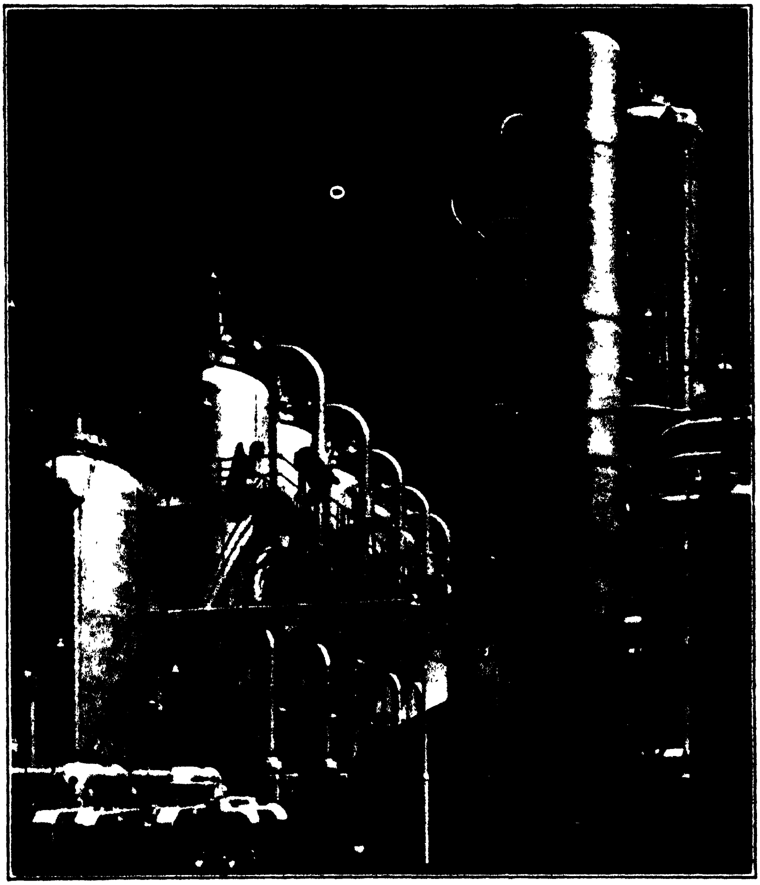
[286] See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

[287] A. P. Vinogradov and G. G. Bergman, *Compt. rend. acad. sci. U.R.S.S.*, 1935, **4**, 349; *Brit. Chem. Abs.* **A**, 1936, 701; *Chem. Abs.*, 1936, **30**, 4655.

[288] Asphaltite is a species of naturally-occurring bitumen. See H. Abraham, "Asphalts and Allied Substances," Third Edition, D. Van Nostrand Co., Inc., New York, 1932.

[289] E. Longobardi, *Anales soc. scient. Argentina*, 1934, 117 (1), 5; *J. Inst. Pet. Tech.*, 1935, **21**, 132, 127A; *Chem. Abs.*, 1934, **28**, 4577; 1935, **29**, 2699; *Brit. Chem. Abs.* **B**, 1935, 391.

petroleum, lignites, bituminous shales and natural asphalts, the quantities of this element associated with these substances being too great to be explained by its wide diffusion in nature. Longobardi found that San Rafael petroleum analyzed 0.0377 per cent of ash, of which 11.9 per cent was vanadium pentoxide which corresponds to 0.0045 per cent in the petroleum. A lignite from the same locality contained 53 times more vanadium than the petroleum. The investigations of Fester[280a] indicated that the vanadium content in San Rafael petroleum was more or less proportional to the bituminous content, and independent of other organic material. He suggested that vanadium is present as a result of its precipitation, along with iron and nickel, from aqueous solution by means of hydrogen sulphide produced by bacterial decomposition of the original organic deposits.



Courtesy Union Oil Co. of California

FIG. 9.—Plant for Dewaxing with Liquid

The high vanadium content of some petroleum ash, particularly from asphaltic crudes, has been utilized industrially for the recovery of that element. The flue dust from the combustion of Mexican fuel oil in oil-tank ships has been collected and processed in British steelworks.

[280a] See also G. A. Fester and J. Cruellas, *Rev. facultad quim. ind. agr.* (Univ. nacl. litoral), 1934, **3**, 1-35; 1936, **4**, 186; *Chem. Abs.*, 1935, **29**, 6179; 1936, **30**, 7505.

Table 9 gives the limits of composition[290] of the ashes from fourteen Hungarian and one Californian crude oil samples.

TABLE 9.—*Approximate Composition of Ashes from Petroleum.*

Constituent	%	Constituent	%
SiO_2	5.43-60.49	K_2O	0- 1.83
Fe_2O_3	7.71-43.87	Na_2O	0.80-12.36
Al_2O_3	7.51-38.82	Li_2O	0- 0.14
MnO	0.16- 0.47	P_2O_5	0- 0.02
NiO	0.03- 4.35	V_2O_5	0- 5.07
CaO	1.09-11.05	SO_3	1.45-21.04
MgO	0.78- 4.26	Cl	0- 0.20

The ash produced during the combustion of certain oils can be a source of inconvenience owing to the formation of a deposit on the sprayer. This question has been discussed by Seiler,[291] who considers that a proposed ash limit of 0.05 per cent is far too high.

The interesting observation has been made that sulphate-bearing waters suffer reduction to sulphides in contact with paraffin-base oils at temperatures of 30-122°C. even in the absence of bacteria.[292] Analytical methods for the examination of oil field waters have been described by Wood and others.[293]

[290] J. Sürü, *Technikai Kurir*, 1935, 6 (1), 4; *Chem. Abs.*, 1935, **29**, 2699.

[291] K. Seiler, *Pharm. Acta Helv.*, 1933, **8**, 223; *Chem. Abs.*, 1934, **28**, 3568.

[292] C. H. Behre, Jr., and R. K. Summerbell, *Science*, 1934, 79, 39; *Chem. Abs.*, 1934, **28**, 1848; *Brit. Chem. Abs.* **A**, 1934, 276.

[293] D. G. Jones and C. E. Wood, *J. Inst. Pet. Tech.*, 1932, **18**, 817; *Chem. Abs.*, 1933, **27**, 1741. See also A. H. K. Radjy and C. E. Wood, *J. Inst. Pet. Tech.*, 1933, **19**, 845; *Chem. Abs.*, 1934, **28**, 1174. W. R. Wiggins and C. E. Wood, *J. Inst. Pet Tech.*, 1935, **21**, 105, 200; *Chem. Abs.*, 1935, **29**, 3816, 4564.

Chapter 2

Thermal Decomposition of Hydrocarbons

PARAFFIN HYDROCARBONS

The vast amount of fundamental research on various phases of thermal decomposition has resulted in a clearer insight on the complex series of reactions undergone by hydrocarbons when subjected to destructive heat treatment. The practical applications of pyrolysis in the production of various unsaturated and aromatic hydrocarbons are described in subsequent chapters, whereas the object of this chapter is to discuss the topic from the more purely scientific and theoretical viewpoints.

If at first it appears that the numerous investigations have failed in several particulars to illuminate the whole field of pyrolytic reactions, it must be remembered that the subject is a most difficult and complex one, both theoretically and practically. In the cracking of any pure hydrocarbon, the reaction products vary both in kind and amount. The obtaining of any one substance at the expense of the other products depends upon an understanding of the primary and secondary reactions.[1] For some hydrocarbons the primary reactions have been carefully studied, but for any single hydrocarbon the mechanism of the decomposition has not been definitely proved.[2]

According to Travers and Pearce,[3] the results obtained in any process do not represent an ultimate equilibrium; they relate only to a definite but unknown time interval. Other factors being identical, the composition of the product would vary with the time interval, and if any one of these conditions, such as pressure, temperature or concentration is altered, a different set of data results.

Egloff and Wilson[4] have enumerated the difficulties in correlating the data obtained on a single hydrocarbon under different reaction temperatures and contact times. They show that for the same temperature the nature and amounts of the products will vary widely with the contact time, depending on the primary and secondary reactions involved. For the same reaction period, the variation will depend on the energy available at a particular temperature. The significance of these factors may disappear if they are properly adjusted, so that a short contact time and high temperature may give the same products as a longer time and lower temperature. Further accurate data will undoubtedly help to account for the discrepancies encountered and to reconcile certain observations which do not seem to fit into any of the theories so far proposed.[5] The relative stability of the lower paraffins toward pyrolysis has been listed by Egloff and Parrish[6] in the following descending order: methane, ethane, propane, isobutane, butane, neopentane (tetramethylmethane), *n*-pentane, isopentane, *n*-hexane and 2-methylpentane.

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[1] Primary reaction products are those substances formed in the initial stages of the pyrolysis of hydrocarbons at small percentage decompositions. Secondary reaction products are those which are formed by interaction of primary compounds. For a discussion of primary and secondary cracking reactions see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934, 96.

[2] G. Egloff and E. Wilson, *Ind. Eng. Chem.*, 1935, **27**, 917; *J. Inst. Pet. Tech.*, 1935, **21**, 369A; *Brit. Chem. Abs.* **A**, 1935, 1206; *Chem. Abs.*, 1935, **29**, 6203. For a review of the reaction mechanisms, see G. Egloff, "The Reactions of Pure Hydrocarbons," Reinhold Publishing Corp., New York, 1937.

[3] M. W. Travers and T. J. P. Pearce, *J.S.C.I.*, 1934, **53**, 321T; *Chem. Abs.*, 1935, **29**, 1057; *Brit. Chem. Abs.* **A**, 1935, 40.

[4] G. Egloff and E. Wilson, *loc. cit.*

[5] Reviews of pyrolysis have been given by P. K. Frolich and P. J. Wiezevich, *Ind. Eng. Chem.*,

Before discussing the experimental data accumulated on the various types of individual hydrocarbons, it is necessary to describe as briefly as possible the various theories of pyrolysis from a general standpoint. The application of such theories to special cases will be considered afterwards.[7]

THEORY OF FREE RADICALS

The actual existence of free radicals during the thermal treatment of organic compounds has been demonstrated chemically by Paneth and Hofeditz[8] and spectroscopically by Bonhoeffer and Haber[9] and Hogness and Kvalnes.[10] The method of investigation developed by Paneth and his collaborators consists in dissociating gaseous organic materials at low pressures and then passing the gaseous products over metallic mirrors. In this manner, volatile organometallic compounds are formed which can be subsequently identified. In principle, this procedure consists in allowing the free radicals to combine with various metals before the former have time to combine with themselves or with co-existing organic molecules. The experiments have shown that free radicals have an exceedingly short life, their half-period[11] being generally in the magnitude of 10^{-3} second. Rice and his coworkers[12] have applied this procedure to organic compounds, particularly hydrocarbons, heated to 700-1100°C. at low pressures. The radicals identified were methyl ($CH_3—$), ethyl ($C_2H_5—$) and methylene ($CH_2=$). The methyl radical appears to be the chief product of such decompositions. The higher alkyl radicals (except ethyl) could not be detected, probably because of their short life and instantaneous decomposition into unsaturated compounds and smaller free radicals.[13]

The methyl radical reacts with tellurium, selenium, arsenic, antimony, zinc, cadmium, mercury, thallium, lead and bismuth. For identification purposes, the products from tellurium and mercury are of particular value, the former giving dimethyl ditelluride ($CH_3TeTeCH_3$) and the latter dimethyl mercury. Dimethyl

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1935. **27**, 1055; *Brit. Chem. Abs.* **B**, 1935. 980; *J. Inst. Pet. Tech.*, 1935. **21**, 408A; *Chem. Abs.*, 1935, **29**, 7624. G. Egloff and E. Wilson, *Ind. Eng. Chem.*, 1935. **27**, 917; *J. Inst. Pet. Tech.*, 1935. **21**, 369A; *Brit. Chem. Abs.* **A**, 1935. 1206; *Chem. Abs.*, 1935, **29**, 6203. F. I. L. Lawrence, *J. Inst. Pet. Tech.*, 1935, **21**, 790; *Brit. Chem. Abs.* **B**, 1935, 979; *Chem. Abs.*, 1935, **29**, 8305; *J. Inst. Pet. Tech.*, 1935. **21**, 399A. F. E. Frey, *Ind. Eng. Chem.*, 1934, **26**, 198; *Chem. Abs.*, 1934, **28**, 2169; *J. Inst. Pet. Tech.*, 1934, **20**, 158A; *Brit. Chem. Abs.* **B**, 1934, 438. E. Audibert, *Ann. combustibles liquides*, 1933, **8**, 565; *Chem. Abs.* 1934, **28**, 463. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**, Chapter 2.

[6] G. Egloff and C. I. Parrish, *Chem. Rev.*, 1936, **19**, 145; *Chem. Abs.*, 1937, **31**, 94; *J. Inst. Pet. Tech.*, 1937, **23**, 22A.

[7] For a brief discussion of the thermodynamic relations between the equilibrium constant, heat of reaction and entropy and free energy changes in a system and applications to a number of reactions involving the thermal decomposition of hydrocarbons, also the heat of activation and the use of this concept, reference should be made to M. W. Travers, *J. Inst. Fuel*, 1935, **8**, 157; *Brit. Chem. Abs.* **B**, 1935, 391; *Chem. Abs.*, 1935. **29**, 7935.

[8] F. Paneth and W. Hofeditz, *Ber.*, 1929, **62**, 1335; *Brit. Chem. Abs.* **A**, 1929, 788; *Chem. Abs.*, 1929, **23**, 5159.

[9] K. F. Bonhoeffer and F. Haber, *Z. physik. Chem.*, 1928, **A137**, 263; *Chem. Abs.*, 1929, **23**, 772; *Brit. Chem. Abs.* **A**, 1929, 11.

[10] T. R. Hogness and H. M. Kvalnes, *Phys. Rev.*, 1928, **32**, 943; *Chem. Abs.*, 1929, **23**, 2650; *Brit. Chem. Abs.* **A**, 1929. 242.

[11] In a unimolecular reaction, the rate of decomposition is proportional to the concentration of substance remaining. In this type of reaction, the time of half-life, or the period of time required for one half of the quantity of material to decompose, is taken as standard. See F. O. Rice and H. C. Urey, "Reaction Velocity in Homogeneous Systems" in H. S. Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York, **1930**. 949. Also F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, **1935**, 56.

[12] F. O. Rice, W. R. Johnston and B. L. Evering, *J.A.C.S.*, 1932, **54**, 3529; *Brit. Chem. Abs.* **A**, 1932, 1108; *Chem. Abs.*, 1932, **26**, 5289. F. O. Rice and M. D. Dooley, *J.A.C.S.*, 1933, **55**, 4245; *Brit. Chem. Abs.* **A**, 1933, 1269; *Chem. Abs.*, 1933, **27**, 5713. F. O. Rice and W. R. Johnston, *J.A.C.S.*, 1934, **56**, 214; *Chem. Abs.*, 1934, **28**, 1655; *Brit. Chem. Abs.* **A**, 1934, 276.

[13] F. O. Rice, *Trans. Faraday Soc.*, 1934, **30**, 152; *Chem. Abs.*, 1934, **28**, 2319; *Brit. Chem. Abs.* **A**, 1933, 1270.

ditelluride is a deep red liquid freezing at −19.5°C. and boiling at 196°C. (with decomposition), comparatively stable in air, insoluble in water but soluble in most organic reagents.[14] Dimethyl mercury will react with alcoholic mercuric bromide to give methyl mercuric bromide, melting at 160°C.[15]

The methylene radical is formed when azomethane is decomposed below 500°C. in a current of diethyl ether or butane. It combines with tellurium, selenium, arsenic and antimony. The product of the action of methylene radical on tellurium is a polymer of telluroformaldehyde, $(CH_2{=}Te)_n$, a red solid of low vapor pressure and insoluble in the usual organic reagents.[16] Evidence gathered by Belchetz and Rideal shows that telluroformaldehyde is readily reduced to dimethyl telluride and dimethyl ditelluride.[17] For this reason the use of iodine was preferred for the detection of methylene radicals, methylene di-iodide being formed even at −65°C. The methylene radical does not combine with zinc, cadmium,[18] mercury, thallium, lead or bismuth.

Active particles consisting of atomic hydrogen, which might conceivably be formed during pyrolysis of hydrocarbons, have been shown not to attack zinc, cadmium or lead mirrors. The possibility of the formation of free radicals of the ethylene type ($-CH_2CH_2-$) has been suggested by Hurd[19] but attempts by Rice and Whaley[20] to isolate them were negative, perhaps due to an exceedingly short life period or to non-interaction with the metallic mirrors used. Experiments to isolate the ethylidene radical ($CH_3CH{=}$) likewise proved unsuccessful.[21]

The Paneth effect may be utilized to determine experimentally activation energies for the dissociation of hydrocarbons into free radicals. If the material under examination is pyrolyzed under low pressure at two or more temperatures, the concentration of free radicals (at the end of the reaction tube) in each case can be measured from the times of disappearance of standard antimony mirrors. If t_1 and t_2 are the observed times at the temperatures T_1 and T_2 (in degrees absolute), the activation energy, E, can be calculated from the formula,

$$\log_e \frac{t_1}{t_2} = \frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The above method has been employed by Rice and Johnston[22] in the case of ethane, propane, *n*-butane, *n*-pentane and *n*-heptane, the values of E for these hydrocarbons being 79.5, 71.5, 65.4, 64.0 and 63.2 kg.-cal. per mole, respectively.

It has been shown by Rice and Herzfeld[23] that the monomolecular character of the pyrolysis of ethane and other hydrocarbons is consistent with a chain mechanism involving free radicals.[24] The essential condition is that the chain shall be terminated by a reaction between "two different carriers of the chain."

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[14] F. O. Rice and A. L. Glasebrook, *J.A.C.S.*, 1934, **56**, 2472; *Brit. Chem. Abs.* **B**, 1935, 62; *Chem. Abs.*, 1935, **29**, 723.

[15] F. O. Rice and B. L. Evering, *J.A.C.S.*, 1934, **56**, 2105; *Chem. Abs.*, 1935, **29**, 447; *Brit. Chem. Abs.* **A**, 1934, 1341.

[16] F. O. Rice and A. L. Glasebrook, *J.A.C.S.*, 1934, **56**, 2381; *Brit. Chem. Abs.* **A**, 1935, 62; *Chem. Abs.*, 1935, **29**, 723. As indicative of the fugitive character of these radicals, it is of interest to note that when decomposition is carried out at 650°C., only methyl radicals are formed.

[17] L. Belchetz and E. K. Rideal, *J.A.C.S.*, 1935, **57**, 1168; *J. Inst. Pet. Tech.*, 1935, **21**, 336A; *Chem. Abs.*, 1935, **29**, 6128; *Brit. Chem. Abs.* **A**, 1935, 1085.

[18] Curiously enough F. O. Rice and F. R. Whaley (*J.A.C.S.*, 1934, **56**, 1311; *Chem. Abs.*, 1934, **28**, 6697; *Brit. Chem. Abs.* **A**, 1934, 863) report that the fragments formed in the electrical decomposition of various organic compounds did not, for some unexplained reason, react with zinc or cadmium mirrors despite the fact that they were shown to consist partly of methyl radicals.

[19] C. D. Hurd, *Ind. Eng. Chem.*, 1934, **26**, 50; *Chem. Abs.*, 1934, **28**, 1014; *Brit. Chem. Abs.* **B**, 1934, 228.

[20] R. O. Rice and F. R. Whaley, *loc. cit.* F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, 1935.

[21] F. O. Rice and A. L. Glasebrook, *J.A.C.S.*, 1934, **56**, 741; *Brit. Chem. Abs.* **A**, 1934, 508; *Chem. Abs.*, 1934, **28**, 2672.

[22] F. O. Rice and W. R. Johnston, *J.A.C.S.*, 1934, **56**, 214; *Chem. Abs.*, 1934, **28**, 1655; *Brit. Chem. Abs.* **A**, 1934, 276. F. O. Rice, *Trans. Faraday Soc.*, 1934, **30**, 152; *Chem. Abs.*, 1934, **28**, 2319; *Brit. Chem. Abs.* **A**, 1933, 1270.

[23] F. O. Rice and K. F. Herzfeld, *J.A.C.S.*, 1934, **56**, 284; *Brit. Chem. Abs.* **A**, 1934, 369; *Chem. Abs.*, 1934, **28**, 1655.

From observations employing a molecular beam[25] method, Beeck[26] substantiates the free radical theory. Using a platinum or carbon filament covered with a unimolecular layer of water at 1550°C., he found that hydrocarbons (except methane) are completely decomposed in primary reactions, indicating the formation of free radicals by the rupture of carbon bonds. Methane, however, dissociated into the free methylene radical and hydrogen under these conditions. Beeck believes that dehydrogenation of paraffin and olefin hydrocarbons cannot occur unless traces of water or of another non-metallic hydride such as hydrogen sulphide are present, and that this unimolecular layer on the catalytic surface is the true seat of dehydrogenation. Bone[27] contends that in the pyrolysis of the lower hydrocarbons it is necessary to assume the primary formation of free radicals such as methylene, methenyl ($CH\equiv$) and methyl. The evidence is based on spectrographic data obtained in combustion of methane, ethane, ethylene and acetylene.

OTHER THEORIES OF PYROLYSIS

Kassel[28] has proposed a theory based on fundamental valence considerations to account for the production of more than two molecules per molecule of higher paraffin hydrocarbon decomposed. It is assumed that, in the case of *n*-butane for example, two hydrogen atoms at opposite ends of the carbon chain are brought into close proximity and united to yield a hydrogen molecule. The resulting carbon chain is broken in the center to furnish two molecules of ethylene. In the same way, *n*-pentane may yield methane and two ethylene molecules. This theory, which ignores the rôle of free radicals, does not agree with experimental data on the two hydrocarbons cited.

Criegee[29] believes that the thermal rupture of carbon chains occurs by removal of hydrogen atoms in the 1,4 position, the resulting 1,4-di-radical undergoing stabilization by cleavage between atoms 2 and 3. The decomposition of *n*-butane is interpreted in the light of this theory as follows:

$$CH_3CH_2CH_2CH_3 \longrightarrow H_2 + -CH_2CH_2CH_2CH_2- \longrightarrow H_2 + 2CH_2{=}CH_2$$

METHANE

Despite considerable experimental work on the thermal decomposition of methane the exact course of the reaction is still doubtful. Primary dissociation to methylene has previously been shown by Kassel[30] and Storch.[31] Belchetz[32] substantiated these findings by passing methane at 0.1 mm. pressure over a platinum filament heated to 877 to 1027°C. and then over mirrors located 3 mm. from the filament. Since the free radicals combined with iodine mirrors to form methylene iodide and with tellurium to furnish a compound decomposable with bromine to give methylene bromide, Belchetz concluded that the reaction must be

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[24] For a discussion of chain reactions, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934, 55.

[25] A discussion of molecular beams has been given by J. B. Taylor (*Ind. Eng. Chem.*, 1931, **23**, 1228; *Chem. Abs.*, 1932, **26**, 346). According to this investigator, they consist of a narrow ray of molecules moving in a unidirectional motion and are formed by passage of molecules through a slit or series of slits in a highly evacuated apparatus.

[26] O. Beeck, *Nature*, 1935, **136**, 1028; *Brit. Chem. Abs.* **A**, 1936, 169; *Chem. Abs.*, 1936, **30**, 1291.

[27] W. A. Bone, *Trans. Faraday Soc.*, 1934, **30**, 148; *Brit. Chem. Abs.* **A**, 1934, 259; *Chem. Abs.*, 1934, **28**, 2319.

[28] L. S. Kassel, *J. Chem. Phys.*, 1933, **1**, 749; *Chem. Abs.*, 1934, **28**, 463; *Brit. Chem. Abs.* **A**, 1934, 54; *Chem. Rev.*, 1932, **10**, 11; *Chem. Abs.*, 1932, **26**, 2367.

[29] R. Criegee, *Ber.*, 1935, **68**, 665; *Brit. Chem. Abs.* **A**, 1935, 727; *Chem. Abs.*, 1935, **29**, 3975.

[30] L. S. Kassel, *J.A.C.S.*, 1932, **54**, 3949; *Chem. Abs.*, 1932, **26**, 5797; *Brit. Chem. Abs.* **A**, 1932, 1209.

[31] H. H. Storch, *J.A.C.S.*, 1932, **54**, 4188; *Chem. Abs.*, 1933, **27**, 15; *Brit. Chem. Abs.* **A**, 1933, 32. See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934, 43, for a discussion of this work.

[32] L. Belchetz, *Trans. Faraday Soc.*, 1934, **30**, 170; *Chem. Abs.*, 1934, **28**, 2321; *Brit. Chem. Abs.* **A**, 1933, 1270.

$$CH_4 \longrightarrow CH_2 + H_2$$

The dimerization of methylene radicals on a cooled glass surface yielded ethylene, which further substantiated this proposed mechanism.

In direct opposition to these results, Rice and Dooley[33] observed that only methyl radicals (identified as dimethyl ditelluride) were formed when using a quartz tube at 1200°C. with the tellurium mirror located 1 cm. from the end of the furnace tube. Belchetz's experiments could not be verified, for in the range of temperature (877-1027°C.) no mirror removal was experienced, even when using a larger reaction tube with and without platinum. Rice and Dooley consider that the primary rupture may be represented by:

$$CH_4 \longrightarrow CH_3 + H \quad \text{and} \quad H + CH_4 \longrightarrow H_2 + CH_3$$

These conflicting results have been discussed by Kassel[34] who has shown that the experimental kinetics of the methane decomposition cannot be explained by any mechanism which involves methyl radicals but are perfectly explicable on the assumption that methylene radicals are the primary intermediates. It should be noted that the mechanism of Rice and Dooley involves the production of atomic hydrogen, but these investigators were unable to detect the latter and concluded that the hydrogen atoms initially formed recombine on the walls or react with methane before reaching the mirror. Kassel has pointed out that the non-appearance of hydrogen atoms in the products of pyrolysis is evidence against the mechanism of Rice and Dooley.

Belchetz and Rideal[35] have since demonstrated rather conclusively that methylene radicals are formed in a dynamic or kinetic system at low pressures in contact with carbon and platinum filaments at temperatures of 1100° to 1750°C. The methylene radicals were identified by reaction with iodine to yield methylene diiodide. It was further shown that, owing to the instability and ease of reduction of telluroformaldehyde, the tellurium test for methylene radicals is somewhat unsatisfactory. The gaseous products obtained by passage of methane at high velocity and a pressure of 0.1 mm. over a carbon filament at 1745°C. contained 17 per cent ethane and 2.7 per cent ethylene. The energy of activation for the decomposition of methane on a carbon filament was found to be 95,000 cal.

It is apparent that further work is necessary before the mechanism of the primary dissociation of methane can be properly elucidated but there is no doubt that formation of highly reactive free radicals, either methyl, methylene, or both, represents the initial step and that recombination of these radicals or reaction with methane gives rise to the observed products, namely, ethane, ethylene and acetylene.

It has been stated by Kobozev, Kashtanov and Kobrin[36] that the velocity constants for the formation of ethylene and acetylene from methane (diluted with 40 per cent of nitrogen) in quartz and porcelain tubes at 1160°C. are independent of the reaction chamber materials and are unaffected by the addition of mercury, bichloride of mercury, sodium or sulphur. Although the rate of ethylene formation is considerably reduced by the presence of antimony and sodium chloride, this is attributed to side reactions rather than catalytic poisoning. The rate of carbon formation, however, is 50 to 100 times greater in quartz than in porcelain and is further accelerated by deposition of carbon in the reaction tube. Mercury vapors act as inhibitors for this reaction, but although bichloride of mercury and sulphur are similar to mercury in their action in a porcelain chamber, nevertheless they do effect an increase in the rate of decomposition of methane in quartz vessels. Finkel'shtein and Zabolotzkii[37] noted that a 95 per cent carbonization of methane could be obtained at 1000°C. using a catalyst of fire clay containing 12 per cent nickel monoxide, 2 per cent chromic oxide and 3 per cent copper oxide. This material is not poisoned by hydrogen sulphide and can be used repeatedly if the carbon is removed by superheated steam.

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[33] F. O. Rice and M. D. Dooley. *J.A.C.S.*, 1934, **56**, 2747; *J. Inst. Pet. Tech.*, 1935, **21**, 47A; *Brit. Chem. Abs.* **A**, 1935, 191; *Chem. Abs.*, 1935, **29**, 723.

[34] L. S. Kassel. *J.A.C.S.*, 1935, **57**, 833; *Brit. Chem. Abs.* **B**, 1935, 827; *J. Inst. Pet. Tech.*, 1935, **21**, 252A; *Chem. Abs.*, 1935, **29**, 4325.

[35] I. Belchetz and E. K. Rideal. *J.A.C.S.*, 1935, **57**, 1168; *J. Inst. Pet. Tech.*, 1935, **21**, 336A; *Chem. Abs.*, 1935, **29**, 6128; *Brit. Chem. Abs.* **A**, 1935, 1085.

[36] N. I. Kobozev, L. I. Kashtanov and S. M. Kobrin. *J. Gen. Chem. (U.S.S.R.)*, 1935, **5**, 143; *Chem. Abs.*, 1935, **29**, 4920; *Brit. Chem. Abs.* **B**, 1935, 714.

The application of the glow discharge method to the cracking of methane was investigated by Kobozev, Vasil'ev and Gal'braikh.[38] Electrodes of aluminum, copper, zinc, lead or iron brought about a conversion of 1.5 per cent of the methane into ethylenic or acetylenic compounds, but when mercury electrodes were substituted under the same conditions the conversion was 5.2 per cent. By warming the electrodes or employing intermediate mercury electrodes, this can be increased to 14 per cent. The effect is ascribed to an activation of the mercury vapor, from which the energy is transferred to the methane molecule.

Kobayashi and others[39] have studied the range 800° to 1300°C. and found that at 1200°C. a maximum yield of ethylene (4 per cent) is obtained. Above this temperature the production of ethylene is lowered and that of acetylene increases reaching 17.4 per cent at 1300°C. The time of contact when varied between 0.05 and 0.15 second was found to have very little effect. Tropsch and Egloff[40] observed that the time factor is extremely important. At 1400°C. and 50 mm. pressure the production of ethylene falls off from 2.2 to 1.2 per cent when the contact time is increased from 0.0023 to 0.0141 second. Acetylene formation is favored, however, going from 1.6 to 6.0 per cent over the same range of time. Lowering the pressure has a like effect according to Frost[41] who obtained a 95 per cent conversion at 1800°K. (1527°C.) and one atmosphere and again at 1500°K. (1227°C.) and 0.1 atmosphere.

The influence of various contact materials on the production of acetylene at high temperatures has been studied by Klyukvin and Klyukvina.[42] Without catalysts at 1250°C., the yields did not exceed 4.2 per cent of the total methane passed or 11.2 per cent of the total reacting methane. When employing vanadium at 1050°C., the corresponding figures were 3.5 and 48.3 per cent respectively. The best coarse catalyst was kaolin which yielded 1.7 per cent acetylene on the methane passed and 16.9 per cent on the methane consumed at 1050°C. Wulff[43] recommends packing the reaction chamber with silicon carbide (Carborundum) particles. Introduction of methane and air at 1400°C. gave 5 to 6 per cent of acetylene. Fischer and Pichler suggest passing a mixture of methane and oxygen through a

[37] V. S. Finkel'shtein and T. V. Zabolotzkii, *Ukrain. Khem. Zhur.*, 1934, **9**, 263; *Brit. Chem. Abs.* **B**, 1935, 258; *Chem. Abs.*, 1935, **29**, 6023.

[38] N. I. Kobozev, S. S. Vasil'ev and E. E. Gal'braikh, *Compt. rend. acad. sci. U.R.S.S.*, 1935 **2**, 236; *Brit. Chem. Abs.* **A**, 1935, 943; *Chem. Abs.*, 1935, **29**, 6152.

[39] K. Kobayashi, K. Yamamoto, H. Ishikawa and S. Hinonishi, *J. Soc. Chem. Ind., Japan*, 1935, **38**, 550 (*Suppl. bind.*); *Brit. Chem. Abs.* **B**, 1936, 133; *Chem. Abs.*, 1936, **30**, 1210.

[40] H. Tropsch and G. Egloff, *Ind. Eng. Chem.*, 1935, **27**, 1063; *J. Inst. Pet. Tech.*, 1935, **21**, 408A; *Brit. Chem. Abs.* **B**, 1935, 1035; *Chem. Abs.*, 1935, **29**, 7935.

[41] A. V. Frost, *Materials on Cracking and Chemical Treatment of Products Obtained, Khimteoret*, 1935, 2, 98; *Chem. Abs.*, 1935, **29**, 5626.

[42] N. A. Klyukvin and S. S. Klyukvina, *Khim. Tverdogo Topliva*, 1935, **6**, 130; *Chem. Abs.*, 1935, **29**, 7617; *Brit. Chem. Abs.* **B**, 1937, 106.

[43] R. G. Wulff U. S. P. 1,917,627, July 11, 1933; *Brit. Chem. Abs.* **B**, 1934, 489; *Chem. Abs.*, 1933, **27**, 4656.

reaction tube heated above 1000° with a contact time of less than 0.01 second.[44] This results in partial combustion with the formation of acetylene and hydrocarbons of a higher carbon content. Thus the optimum yields of acetylene are 6.2 per cent at 1000°C. with 0.0085 second contact time, and 6.6 per cent at 1600°C. with 0.0029 second. Longer periods of heating, however, cause a decreased conversion.

Methane may be converted into liquid hydrocarbons by heat treatment between 400° and 1100°C. in the presence of mercury or cadmium vapors.[45] A yield of 12 g. of tar and 12 ml. of oil per cubic meter of methane was obtained by Oda[46] who used quartz tubes of 3 to 15.5 mm. internal diameter and catalysts of silica and pumice stone with and without ferric oxide and nickel. By diluting the methane with hydrogen the yield of oil and tar was lowered, even when larger reaction tubes, higher temperatures and longer heating periods were employed. Dilution of the feed gas with oxygen resulted in partial combustion with a negligible formation of tar and oil.

ETHANE

The main reaction in the early stages of decomposition of ethane is one of dehydrogenation to ethylene, which occurs without catalysts at about 650°. Rice has suggested a mechanism involving the decomposition to two methyl radicals[47] which then initiate chain reactions. Sachsse[48] determined the concentration of hydrogen atoms produced during the thermal decomposition of ethane at 560 to 590°C. to be twice as great as corresponds with the equilibrium value for the dissociation of pure hydrogen. This shows that part of the ethane decomposes primarily into methyl radicals which form hydrogen atoms by chain reactions. However, it was also pointed out that the concentration of hydrogen atoms is only about 0.001 of the value calculated according to the Rice theory, which holds that all the ethane decomposes by chain reactions initiated by the formation of methyl radicals. Sachsse concluded, therefore, that only a small part of the ethane decomposes primarily into radicals.

Belchetz and Rideal,[49] in studying the decomposition of ethane at low pressures in contact with carbon filaments at 1450 to 1800°C., have failed to obtain any evidence of the formation of methyl or ethylidene radicals. The very close agreement between the activation energy of 94.6 kg.-cal. for this reaction and that obtained for methane (95 kg.-cal.) using the same method, suggests the possibility that the same process is involved, that of the removal of two hydrogen atoms as a molecule from the same carbon atom as first suggested by Kassel.[50] If this is the mechanism, the ethylidene radical must undergo tautomeric conversion to ethylene immediately after formation. However, Belchetz and Rideal consider it much more likely that ethylene is the primary product.

The decomposition of a molecular beam of ethane projected on to a hot plati-

[44] F. Fischer and H. Pichler, U. S. P. 1,940,209, Dec. 19, 1933; *Chem. Abs.*, 1934, **28**, 1353; *Brit. Chem. Abs.* **B**, 1934, 917.

[45] F. Winkler and H. Haeuber, U. S. P. 1,986,238 and 1,986,239, Jan. 1, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1098.

[46] R. Oda, *J. Soc. Chem. Ind., Japan*, 1934, **37**, 630 (*Suppl. bind.*); *Chem. Abs.*, 1935, **29**, 1073; *J. Inst. Pet. Tech.*, 1935, **21**, 49A.

[47] R. O. Rice, *J.A.C.S.*, 1931, **53**, 1959; *Chem. Abs.*, 1931, **25**, 2967; *Brit. Chem. Abs.* **A**, 1931, 819. Reference should be made to Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**, 47, for a discussion of this theory.

[48] H. Sachsse, *Z. physik. Chem.*, 1935, **B31**, 79; *Brit. Chem. Abs.* **A**, 1936, 432; *Chem. Abs.*, 1936, **30**, 2471.

[49] L. Belchetz and E. K. Rideal, *J.A.C.S.*, 1935, **57**, 1168; *J. Inst. Pet. Tech.*, 1935, **21**, 336A; *Chem. Abs.*, 1935, **29**, 6128; *Brit. Chem. Abs.* **A**, 1935, 1085.

[50] L. S. Kassel, *Chem. Rev.*, 1932, **10**, 11; *Chem. Abs.*, 1932, **26**, 2367.

TABLE 11.—*Pyrolysis of Ethane at 50 mm. Pressure.*

Temperature, °C.	1100					1400				
Contact time, 10^{-3} sec.	1.53	2.22	2.48	5.85	10.5	0.28	0.41	0.88	1.64	9.50
Gas analysis, %										
C_2H_2	3.4	2.2	2.2	4.0	4.8	3.2	4.8	12.0	17.8	15.4
C_2H_4	28.4	32.2	33.4	30.6	27.4	30.2	32.8	20.6	5.0	0.4
C_2H_6	4.2	4.2	2.2	2.4	2.8	2.2	1.4	0.6	0.0	0.0
C_nH_{2n+2}	—	—	—	—	—	25.8	13.4	12.2	—	4.9
H_2	—	—	—	—	—	34.6	41.2	5.2	—	70.7
n of Paraffins*	—	—	—	—	—	1.7	1.3	1.1	—	1.0
C formed, % of total C charged	—	—	—	—	—	0.0	0.3	8.0	—	44.0
Liters of product per 100 l. ethane charged										
C_2H_2	5.4	4.0	4.1	8.5	10.6	5.5	9.8	27.3	36.7	47.8
C_2H_4	45.2	59.0	62.0	64.5	60.7	52.0	67.3	46.8	28.6	1.2
C_2H_6	6.7	7.7	4.1	5.1	6.2	3.8	2.9	1.4	0.0	0.0

* Average number of carbon atoms per molecule

of ethylene at 900-950°C., the proportion increasing with the rate of flow. Decomposition of ethylene to acetylene occurred above 830°C. Also, it was noted

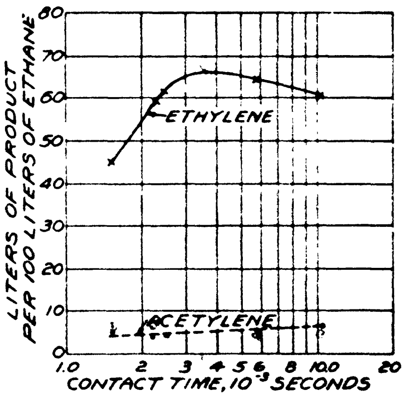

FIG. 10.
Pyrolysis of Ethane at 1100°C. and 50 mm. Pressure. (H. Tropsch and G. Egloff)

Courtesy Industrial and Engineering Chemistry

that some liquid products were formed by polymerization of butadiene and acetylene resulting from dehydrogenation of ethylene.

start

PROPANE

Propane pyrolyzes according to the following schemes at atmospheric pressure:

$$(1)\ C_3H_8 \rightleftharpoons C_3H_6 + H_2$$
$$(2)\ C_3H_8 \longrightarrow C_2H_4 + CH_4$$
$$\text{and}\ (3)\ 2C_3H_8 \longrightarrow C_3H_6 + C_2H_6 + CH_4$$

According to Tropsch, Thomas and Egloff,[55] reaction (1) is a true equilibrium and should be suppressed by the application of pressure, whereas (2) should not be influenced.[56] Reaction (3) plays only a small role until the pressure is raised.

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[55] H. Tropsch, C. L. Thomas and G. Egloff, *Ind. Eng. Chem.*, 1936, 28, 324; *Brit. Chem. Abs.* B, 1936, 535; *J. Inst. Pet. Tech.*, 1936, 22, 203A; *Chem. Abs.*, 1936, 30, 3212.

[56] In the first instance, the reversed reaction involves the union of hydrogen and propene to give

Then it should predominate more and more, since it is bimolecular and its rate is proportional to the concentration of the substance undergoing change. This reaction is thermodynamically possible and also probable, as the calculations of Lang and Morgan[57] on the free energy change give —11,830 cal. at 627°C.

Using a carbon filament at 1650°C., Belchetz and Rideal[57a] were able to identify only propene in the decomposition products. At 1750°C., ethylene was also found. The energy of activation of propane on carbon was calculated to be 94.2 kg.-cal., which is very close to that obtained for methane and ethane by this method.

Dintzes and Frost[57b] have pointed out that the pyrolysis of propane at 616-666°C. in a quartz tube at low pressure does not follow a unimolecular course but probably involves a chain mechanism. Paul and Marek[58] found that dissociation in copper and fused silica tubes is not affected by changes of reactor surface-volume ratio. In the temperature range 550° to 650°C. at atmospheric pressure the relation between the equilibrium constant and the temperature is governed by the equation,

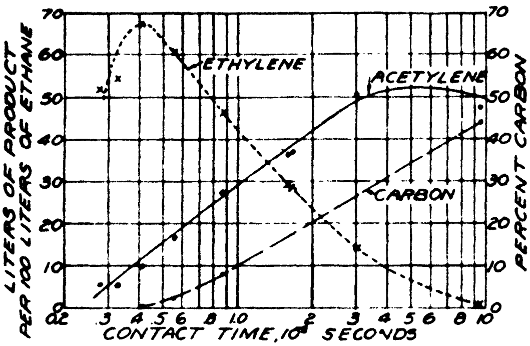

FIG. 11. Pyrolysis of Ethane at 1400° C. and 50 mm. Pressure. (H. Tropsch and G. Egloff)

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$$\log_{10}k = 16.60 - \frac{74850}{2.3RT}$$

The results of Tropsch, Thomas and Egloff[59] indicate that the bimolecular reaction (3) may account for as much as 70 per cent of the propane decomposed at 555-585°C. under a pressure of 725 lb. per sq. in. At 555°C. with a contact time of 95 seconds, the proportions of propane decomposed (about 12 per cent of the total feed) according to reactions (1), (2) and (3) were 6.8, 33.0 and 54.0 per cent, respectively. At 585°C. with 87 seconds contact 0.9 gal. of liquid hydrocarbons per 1000 cu. ft. of gas was obtained and about 30 per cent of the propane was consumed per passage.

The pyrolysis of propane at 600, 650 and 700°C. and under 1 and 7 kg. per sq. cm. pressure has been investigated by Egloff, Thomas and Linn.[60] At the lower

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propane (a hydrogenation process), whereas the second reaction would require a direct union between ethylene and methane molecules, which is not a reversible process, and hence the effect of pressure.

[57] W. Lang and J. J. Morgan, *Ind. Eng. Chem.*, 1935, 27, 937; *J. Inst. Pet. Tech.*, 1935, 21, 370A; *Chem. Abs.*, 1935, 29, 6203; *Brit. Chem. Abs.* A, 1935, 1221.

[57a] L. Belchetz and E. K. Rideal, *J.A.C.S.*, 1935, 57, 2466; *Brit. Chem. Abs.* A, 1936, 169; *J. Inst. Pet. Tech.*, 1936, 22, 86A; *Chem. Abs.*, 1936, 30, 1641.

[57b] A. I. Dintzes and A. V. Frost, *Compt. rend. acad. sci. U.R.S.S.*, 1934, [illegible], 510; *Brit. Chem. Abs.* A, 1934, 1311; *Chem. Abs.*, 1935, 29, 2058.

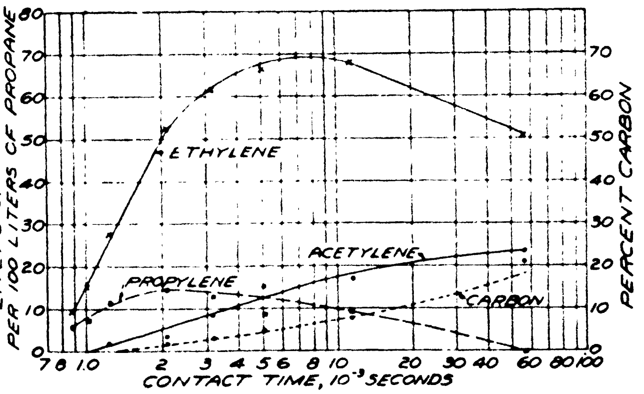
[58] R. E. Paul and L. F. Marek, *Ind. Eng. Chem.*, 1934, 26, 454; *Brit. Chem. Abs.* A, 1934, 603; *Chem. Abs.*, 1934, 28, 3973.

[59] H. Tropsch, C. L. Thomas and G. Egloff, *loc. cit.*

[60] G. Egloff, C. L. Thomas and C. B. Linn, *Ind. Eng. Chem.*, 1936, 28, 1283; *Chem. Abs.*, 1936, 30, 7988; *J. Inst. Pet. Tech.*, 1937, 23, 21A.

pressure, the highest concentration of propene (14 per cent) was attained at 700°C. and 5.4 seconds contact time, with 35 per cent of the propane undergoing decomposition. Optimum conditions for the formation of ethylene at 1 kg. per sq. cm. pressure were at 700°C. and a contact time of 19 seconds, corresponding to a 23.9 per cent content in the exit gas. The application of pressure lowers the proportion of olefins and yields somewhat, but at the same time greatly increases the production rate. The investigators point out that the effect of increasing the reaction time increases the extent of the reaction and also the concentration of unsaturates up to a maximum, after which longer durations caused only a decrease in the latter. It was also noted that the propene maxima point always occurred at shorter contact times than that of ethylene.

In the thermal treatment of propane at 650-860°C. under atmospheric pressure in a steel alloy (Sicromal) tube, it was noted by Schmieden[61] that the highest yields of unsaturates occurred in the range 730-790°C. Thus, at 760°C. with a contact time of 2 seconds a 72 volume per cent yield resulted, one-third of which was propene and higher olefins. Carbon deposition amounted to about 1 per cent (by weight) of the original propane.



Courtesy Industrial and Engineering Chemistry

FIG. 12.—Pyrolysis of Propane at 1100°C. and 50 mm. Pressure. (H. Tropsch and G. Egloff)

A 75-80 per cent yield of unsaturated hydrocarbons (ethylene and propene) was obtained by Frolich and Wiezevich[62] from propane diluted with 70 per cent air and heated to 675°C. for 30 seconds in a copper reactor. Low yields of liquid products resulted with simultaneous cracking and polymerization at 1 atmosphere, and with pyrolysis at 840°C. and 1 atmosphere followed by polymerization at 650°C. and 48 atmospheres pressure. The optimum conversion (7.75 gal. per 1000 cu. ft.) was obtained after cracking by dehydrogenation in the presence of copper oxide and subsequent polymerization at 400°C. and 170 atmospheres.

According to Lang and Morgan,[63] varying the partial pressure of propane by dilution with steam clearly shows the importance of the bimolecular reaction. Experiments were carried out in the range of 600-700°C. at constant rate of contact. Up to pressures of 0.2 atmosphere, methane, ethylene, propene and hydrogen are produced in approximately equal amounts. Above this pressure the production of ethane becomes appreciable and that of ethylene and hydrogen tends to decrease.

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[61] W. Schmieden, *Oel u. Kohle*, 1936, **12**, 930; *Brit. Chem. Abs* **B**, 1937, 20; *J. Inst. Pet. Tech.*, 1937, **23**, 57A.

[62] P. K. Frolich and P. J. Wiezevich, *Ind. Eng. Chem.*, 1935, **27**, 1055; *J. Inst. Pet. Tech.*, 1935, **21**, 408A; *Chem. Abs.*, 1935, **29**, 7624; *Brit. Chem. Abs.* **B**, 1935, 980.

[63] J. W. Lang and J. J. Morgan, *Ind. Eng. Chem.*, 1935, **27**, 937; *J. Inst. Pet. Tech.*, 1935, **21**, 370A; *Chem. Abs.*, 1935, **29**, 6203; *Brit. Chem. Abs.* **A**, 1935, 1221.

The work of Cambron and Bayley[64] indicates the necessity of employing conditions of turbulent flow of gases in hot tubes for optimum formation of intermediate products. High conversions to aromatic hydrocarbons can be obtained by subjecting gaseous propane to turbulent flow through alloy steel tubes (containing 18 per cent of nickel) at temperatures as low as 800°C. under slight positive pressure. Yields of 23.3 lb. of light oil per 1000 cu. ft. of propane passed were obtained at 800°C., together with 10 lb. of liquid boiling above 200°C. The light oil contained 64 per cent benzene, 14 per cent toluene, 7.8 per cent styrene and small proportions of cyclopentadiene, xylenes and higher aromatics. The higher-boiling liquid con-

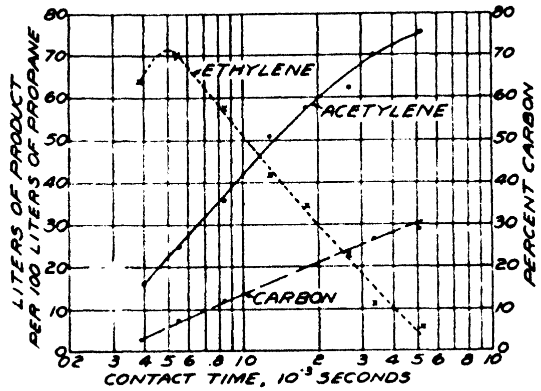

FIG. 13.
Pyrolysis of Propane at 1400°C. and 50 mm. Pressure. (H. Tropsch and G. Egloff)

Courtesy Industrial and Engineering Chemistry

TABLE 12.—*Pyrolysis of Propane at 50 mm. Pressure.*

Temperature, °C.	1100					1400				
Contact time, 10^{-3} sec.	0.877	1.25	3.20	11.5	56.4	0.39	0.85	1.83	3.40	5.23
Gas analysis, %										
C_2H_2	0.0	1.3	4.1	7.2	8.1	7.0	12.6	17.4	20.2	20.6
C_2H_4	8.1	18.7	29.5	28.4	17.8	28.2	20.2	10.4	3.2	1.8
C_3H_6	5.2	7.7	6.2	2.4	0.0	6.4	1.2	0.0	0.0	0.0
C_nH_{2n+2}	74.7	31.3	30.2	27.4	24.8	27.8	22.4	—	15.8	11.8
H_2	7.8	23.6	25.8	31.2	40.6	27.0	39.4	—	57.4	61.2
n of Paraffins[a]	3.03	2.01	1.71	1.22	1.05	1.4	1.0	—	1.0	1.0
C formed, % of total C charged	0.0	2.0	3.0	7.7	21.5	2.3	11.9	—	26.4	28.1
Liters of product per 100 l. of propane charged										
C_2H_2	0.0	1.9	8.6	17.2	23.2	15.9	35.8	57.5	70.0	75.7
C_2H_4	9.5	27.9	61.8	68.0	51.0	64.0	57.5	34.4	5.6	5.6
C_3H_6	6.1	11.8	13.0	9.1	0.0	14.5	3.4	0.0	0.0	0.0

[a] Average number of carbon atoms per molecule.

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[64] A. Cambron and C. H. Bayley, *Can. J. Research*, 1933, 9, 583, 591; 1934, 10, 145; *Brit. Chem. Abs.* B, 1934, 308; *Brit. Chem. Abs.* A, 1934, 507; *Chem. Abs.*, 1934, 28, 1506; *J. Inst. Pet. Tech.*, 1934, 20, 74A.

sisted of 25 per cent naphthalene, 12.5 per cent anthracene, and smaller percentages of mono- and dimethyl-naphthalenes, acenaphthene and phenanthrene. The gaseous products resulting were ethylene (which represented 30 per cent of the propane decomposed, butadiene (about 5 per cent) and small amounts of acetylene.

High-temperature-low-pressure pyrolysis yields large quantities of ethylene and acetylene, as can be seen from the results of Tropsch and Egloff.[65] Table 12.

The striking similarity between the pyrolysis of propane and that of ethane can best be noticed by comparing Figs. 10 and 12 for treatment at 1100°C. and Figs. 11 and 13 for pyrolysis at 1400°C. The maximum yields of ethylene are approximately the same in all four cases, but the contact times are much shorter at the higher temperature. Carbonization is slightly more pronounced in ethane than in propane at 1400°C.

N-BUTANE

In the initial stages of the thermal decomposition of *n*-butane the principal reactions are:

$$\begin{array}{lll}(1)\ n\text{-}C_4H_{10} & \rightleftharpoons & n\text{-}C_4H_8 + H_2 \\ (2)\ n\text{-}C_4H_{10} & \longrightarrow & C_3H_6 + CH_4 \\ (3)\ n\text{-}C_4H_{10} & \longrightarrow & C_2H_4 + C_2H_6\end{array}$$

Reaction (1), accounting for 16 per cent of the products at normal pressure, is a true equilibrium and may be suppressed by increasing the pressure.[66] The others are non-reversible and would not respond to pressure changes. Reaction (2) accounts for 48.5 per cent and (3) for 34.5 per cent of the products at 600°C. and atmospheric pressure.

In addition, two bimolecular reactions have been proposed by Tropsch, Thomas and Egloff. They are:

$$\begin{array}{llll} & (4)\ 2n\text{-}C_4H_{10} & \longrightarrow & n\text{-}C_4H_8 + C_3H_6 + CH_4 \\ \text{and} & (5)\ 2n\text{-}C_4H_{10} & \longrightarrow & n\text{-}C_4H_8 + 2C_2H_6\end{array}$$

The true significance of these latter equations will be discussed subsequently.

The similarity in the primary decomposition of the lower paraffins has been shown by Belchetz and Rideal[67] using a carbon filament heated to 1400° to 2000°C. The energies of activation calculated from the data obtained were: methane, 95, ethane, 94.6, propane, 94.2 and butane, 93.2 kg.-cal. per mole. It was concluded that because of the closeness of these values the primary dissociation must be of the same general type, i.e., the production of molecular hydrogen and the complementary olefin. The latter may decompose to methylene and the next lower olefin. Methylene subsequently undergoes reaction with the surrounding molecules.[68]

The data of Paul and Marek[69] for the limited decomposition of *n*-butane in copper and fused silica tubes show that the reaction at atmospheric pressure is homogeneous and unimolecular, the velocity constants in the temperature range 530-625°C. being represented by the equation:

$$\log_{10}k = 17.05 - \frac{73900}{2.3RT}$$

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[65] H. Tropsch and G. Egloff, *Ind. Eng. Chem.*, 1935, **27**, 1063; *J. Inst. Pet. Tech.*, 1935, **21**, 408A; *Brit. Chem. Abs.* **B**, 1935, 1035; *Chem. Abs.*, 1935, **29**, 7935.

[66] H. Tropsch, C. L. Thomas and G. Egloff, *Ind. Eng. Chem.*, 1936, **28**, 324; *Brit. Chem. Abs.* **B**, 1936, 535; *Chem. Abs.*, 1936, **30**, 3212; *J. Inst. Pet Tech.*, 1936, **22**, 203A.

[67] L. Belchetz and E. K. Rideal, *J.A.C.S.*, 1935, **57**, 1168, 2466; *Brit. Chem. Abs.* **A**, 1936, 169; *J. Inst. Pet. Tech.*, 1936, **22**, 86A; *Chem. Abs.*, 1935, **29**, 6128; 1936, **30**, 1641.

[68] According to L. S. Echols, Jr., and R. N. Pease, (*J.A.C.S.*, 1936, **58**, 1317; *Brit. Chem. Abs* **A**, 1936, 1090; *Chem. Abs.*, 1936, **30**, 5933.), the cracking of propane, n-butane and isobutane at 425°C. is induced by the presence of ethylene oxide. Ethane, however, they report to be unaffected under these conditions.

[69] R. F. Paul and L. F. Marek, *Ind. Eng. Chem.*, 1934, **26**, 454; *Brit. Chem. Abs.* **A**, 1934, 603; *Chem. Abs.*, 1934, **28**, 3973.

Variation of reaction surface-volume ratio, dilution with nitrogen and change of surface from copper to silica were found to have no effect on the reaction velocity.

Hurd, Parrish and Pilgrim[70] have pyrolyzed *n*-butane at low temperatures in empty Pyrex tubes. The primary products at incipient decomposition temperatures included methane, ethane, ethylene, propene and traces of hydrogen. At 365°C., 0.46 per cent dissociation was noted; this was increased to 5 per cent at 415°C. No evidence could be found to support the statement of Norris and Thomson[71] that there is a scission at any specific C-C bond location in the molecule if temperatures near the initial decomposition values are used.

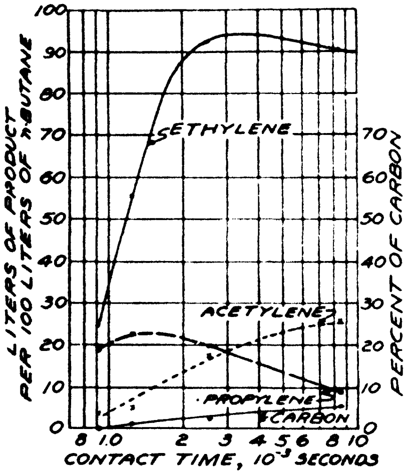

FIG. 14.
Pyrolysis of *n*-Butane at 1100°C. and 50 mm. Pressure. (H. Tropsch and G. Egloff)

Courtesy Industrial and Engineering Chemistry

Over the range 525° to 555°C. at 725 lbs. per sq. in. pressure, Tropsch, Thomas and Egloff[72] found that butane was decomposed in the following manner: 1.4 per cent dehydrogenation to butene according to reaction (1), 33.6 per cent demethylation to propene (2), 30.0 per cent to ethylene and ethane (3), 31.9 per cent to butene, propene and methane (bimolecular) (4), and 3.2 per cent to butene and ethane (bimolecular) (5). The importance of pressure can be seen in that reaction (1), a true equilibrium, was greatly suppressed, the normal value at ordinary pressure in approximately the same temperature range being 16 per cent, whereas the bimolecular reaction (4) which under ordinary conditions is usually negligible, becomes very nearly the predominating one. The following equation for evaluation of contact time was proposed:

$$C = V_r \times 60t \times \frac{273}{T} \times P \times \frac{2}{V' + V^\circ}$$

where C = contact time, in minutes
V_r = volume in cc. of apparatus at reaction temperature
t = total time of experiment, minutes
P = operating pressure, atmospheres
V' = volume in cc. under standard conditions of gas charged to apparatus in time t
V° = volume in cc. under standard conditions of gas and vapor recovered from apparatus in time t
T = absolute temperature

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[70] C. D. Hurd, C. I. Parrish and F. D. Pilgrim, *J.A.C.S.*, 1933, 55, 5016; *J. Inst. Pet. Tech.*, 1934, 20, 162A; *Brit. Chem. Abs.* A, 1934, 167; *Chem. Abs.*, 1934, 28, 737.

[71] J. F. Norris and G. Thomson, *J.A.C.S.*, 1931, 53, 3108; *Chem. Abs.*, 1931, 25, 4842; *Brit. Chem. Abs.* A, 1931, 1147.

[72] H. Tropsch, C. L. Thomas and G. Egloff, *loc. cit.*

This formula was developed assuming that the ideal gas laws hold under these conditions. With the gases ordinarily used, this is nearly true. The greatest error (about 5 per cent) was with *n*-butane at 550°C. and 1000 lbs. per sq. in.

It has been shown by Hurd and Pilgrim[73] that the decomposition of *n*-butane at 600°C. pursues the same course at roughly the same reaction velocity in iron, nickel and quartz tubes. Monel metal, on the other hand, violently catalyzes the decomposition of butanes at 600°C., resulting mainly in complete dissociation to carbon and hydrogen. At 500°C., however, it exerts very little action. Hurd and Pilgrim obtained their time of contact from the formula:

$$t = VT_1/FT_2$$

where t = contact time in minutes, V = volume of the tube in cc., T_1 = absolute temperature of entering gas, T_2 = absolute temperature of heated gas, F = average rate of flow of gas through the tube, cc. per minute. This equation, also based on the ideal gas laws, can be used only at atmospheric pressure. It shows, however, that if the rate of flow and the temperature of the incoming gas are maintained constant, the product of the contact time and reaction temperature will equal a constant value. This explains the fact that the products obtained from *n*-butane at about 400°C. are very similar to those formed at 600° and 700°C. using correspondingly shorter periods of contact.[74]

The pyrolysis of *n*-butane in non-catalytic metal tubes at 600° and 650°C. and at 1 and 7 kg. per sq. cm. pressure has been discussed by Egloff, Thomas and Linn.[75] The concentration of *n*-butene in the exit gas reached a maximum 5 per cent at 750°C., 7 kg. per sq. cm. and a time of contact of about 5 seconds. Propene formation was highest under the same conditions of temperature and pressure, but with heating periods of 18 seconds, amounting to 17.5 per cent by volume of the reaction mixture. On the other hand, the optimum concentration of ethylene was attained at 660°, 1 kg. per sq. cm. and 142 seconds. In these tests, the rates of formation of the olefins at 7 kg. are from 8 to 10 times those at atmospheric pressure. High temperature-low pressure pyrolysis at short contact times distinctly favors the production of ethylene. As mentioned previously, the importance of the duration of the reaction period is stressed by Tropsch and Egloff.[76] Their data, corresponding to 1100°C. and 50 mm. pressure, are given in Table 13.

TABLE 13.—*Pyrolysis of* n-*Butane at 1100°C. and 50 mm. Pressure.*

Contact time, 10^{-3} sec.	0.921	1.26	2.56	8.44
Gas analysis, %				
C_2H_2	2.8	2.5	6.8	9.5
C_2H_4	17.1	28.4	35.8	33.2
C_3H_6	13.2	11.3	7.6	3.2
C_nH_{2n+2}	54.7	38.6	24.9	24.7
H_2	11.5	17.4	22.7	27.0
n of Paraffins[a]	3.56	2.73	1.43	1.26
C formed, % of total C charged	0.0	1.2	2.5	5.7
Liters of product per 100 liters of butane charged				
C_2H_2	3.9	4.9	17.5	25.8
C_2H_4	24.9	55.5	92.3	90.3
C_3H_6	18.6	22.2	19.6	8.7

[a] Average number of carbon atoms per molecule

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[73] C. D. Hurd and F. D. Pilgrim, *J.A.C.S.*, 1933, **55**, 4902; *J. Inst. Pet. Tech.*, 1934, **20**, 162A; *Chem. Abs.*, 1934, **28**, 737; *Brit. Chem. Abs.* **A**, 1934, 167.

[74] C. D. Hurd and F. D. Pilgrim; C. D. Hurd, C. I. Parrish and F. D. Pilgrim, *loc. cit.*

[75] G. Egloff, C. L. Thomas and C. B. Linn, *Ind. Eng. Chem.*, 1936, **28**, 1283; *Chem. Abs.*, 1936, **30**, 7988; *J. Inst. Pet. Tech.*, 1937, **23**, 21A.

[76] H. Tropsch and G. Egloff, *Ind. Eng. Chem.*, 1935, **27**, 1063; *Brit. Chem. Abs.* **B**, 1935, 1035; *Chem. Abs.*, 1935, **29**, 7935; *J. Inst. Pet. Tech.*, 1935, **21**, 408A.

Tropsch and Egloff believe the cracking into ethane and ethylene to be the primary reaction, and dehydrogenation to ethylene a secondary one, although with short contact times it seems to them more probable that the decomposition is to 2 molecules of ethylene and 1 of hydrogen, in accordance with the views of Criegee.[77]

The relations between the yield of products and contact time are shown in Fig. 14. Ethylene formation is the greatest with this hydrocarbon, being about 33 per cent more than in the case of ethane or propane. Under similar conditions, acetylene and propene are produced in greater amounts than when using propane but carbonization proceeds to about the same extent.

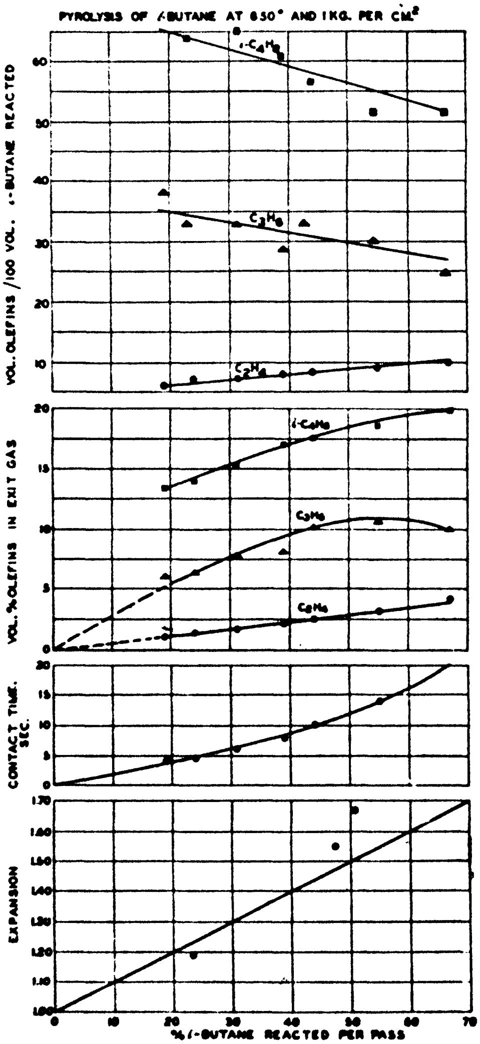

FIG. 15. Pyrolysis of Isobutane at 650°C. and 1 kg. per sq. cm. (G. Egloff, C. L. Thomas and C. B. Linn)

Courtesy Industrial and Engineering Chemistry

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[77] R. Criegee, *Ber.*, 1935, **68**, 665; *Brit. Chem. Abs.* **A**, 1935, 727; *Chem. Abs.*, 1935, **29**, 3975. His views have been discussed in the introduction to this chapter.

ISOBUTANE

The two main primary reactions occurring in the thermal decomposition of isobutane may be represented by the equations:

$$(1)\ iso\text{-}C_4H_{10} \longrightarrow iso\text{-}C_4H_8 + H_2$$
$$\text{and}\ (2)\ iso\text{-}C_4H_{10} \longrightarrow C_3H_6 + CH_4$$

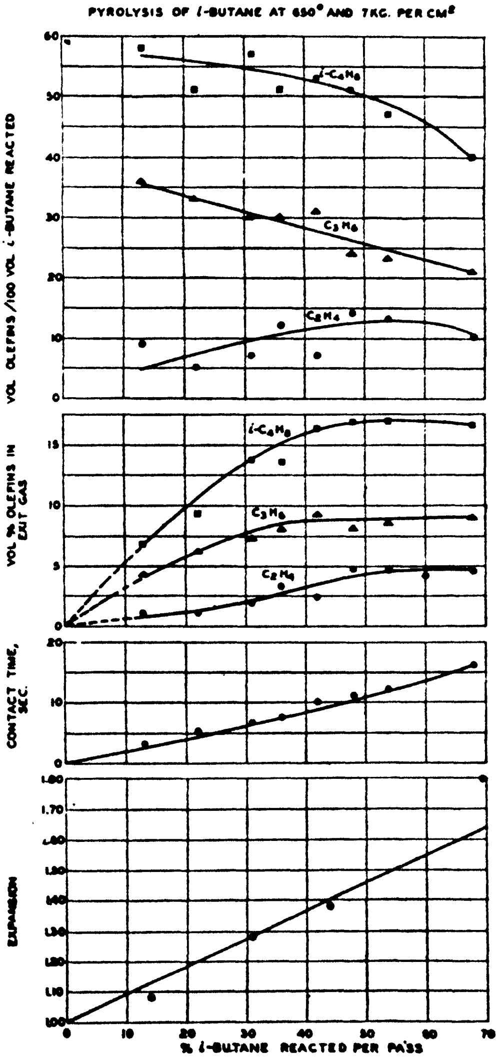


FIG. 16.
Pyrolysis of Isobutane at 650° C. and 7 kg. per sq. cm. (G. Egloff, C. L. Thomas and C. B. Linn)

Courtesy Industrial and Engineering Chemistry

In addition, according to Tropsch, Thomas and Egloff,[78] there is also a bimolecular reaction,

$$(3)\ 2\ iso\text{-}C_4H_{10} \longrightarrow iso\text{-}C_4H_8 + C_3H_8 + CH_4$$

---

[78] H. Tropsch, C. L. Thomas and G. Egloff, *Ind. Eng. Chem.*, 1936, **28**, 324; *Brit. Chem. Abs.* B, 1936, 535; *J. Inst. Pet. Tech.*, 1936, **22**, 203A; *Chem. Abs.*, 1936, **30**, 3212.

which becomes very prominent at high pressures. At 555°C. and 725 lbs. per sq. in. pressure, only 5.9 per cent decomposes according to equation (1), whereas reactions (2) and (3) represent 37.8 and 39.9 per cent of the dissociation. Small amounts of ethylene and ethane were also formed.

The velocity of dissociation at 550° to 610°C. under atmospheric pressure has been investigated by Paul and Marek.[79] As in the case of *n*-butane, the reaction is homogeneous and unimolecular, and is unaffected by change of surface or by dilution with nitrogen. Under conditions of limited decomposition, the velocity constant and temperature are related by the equation:

$$\log_{10} k = 14.89 - \frac{66{,}040}{2.3RT}$$

The results of Egloff, Thomas and Linn[80] on the dissociation of isobutane at 650°C. and pressures of 1 and 7 kg. per sq. cm. are represented graphically in Figs. 15 and 16, respectively. From the latter figure, it will be seen that the maximum concentration of isobutene in the exit gas was 17 per cent, corresponding to a yield of 45 per cent with a 12 second heating time. On the other hand, at 1 kg. per sq. cm. pressure, the optimum content is about 21 per cent at 21 seconds. The proportion of propene reaches its greatest value (12 per cent) at the lower pressure with a contact period of 39 seconds.

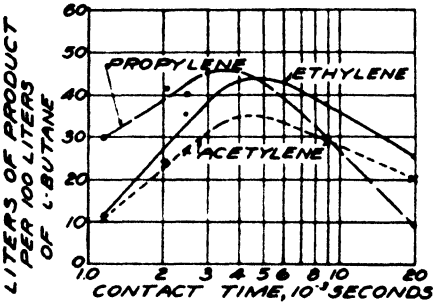


FIG. 17.
Pyrolysis of Isobutane at 1100°C. and 50 mm. Pressure. (H. Tropsch and G. Egloff)

Courtesy Industrial and Engineering Chemistry

High-temperature pyrolysis of isobutane takes a different path from that of the normal gaseous paraffins under the same conditions, propene and acetylene being formed in higher yields in this case. Tropsch and Egloff[81] have investigated the decomposition at 1100°C. and 50 mm. pressure. Their data are given in Table 14.

TABLE 14.—*Pyrolysis of Isobutane at 1100°C. and 50 mm. Pressure.*

Contact time, 10^{-3} sec.	1.14	2.03	2.50	8.85	19.8
Gas analysis, %					
C_2H_2	6.9	10.8	11.0	10.6	8.8
C_2H_4	7.4	11.0	14.0	14.0	11.0
C_3H_6	19.0	18.8	16.6	10.8	4.0
iso-C_4H_8	4.8	0.0	0.0	0.0	0.0
Liters of product per 100 liters isobutane					
C_2H_2	10.9	24.0	26.6	28.7	20.4
C_2H_4	11.7	24.4	35.4	37.9	25.5
C_3H_6	30.0	41.7	40.2	29.3	9.3
iso-C_4H_8	7.6	0.0	0.0	0.0	0.0

[79] R. E. Paul and L. F. Marek, *Ind. Eng. Chem.*, 1934, 26, 454; *Chem. Abs.*, 1934, 28, 3973; *Brit. Chem. Abs.* A, 1934, 603.

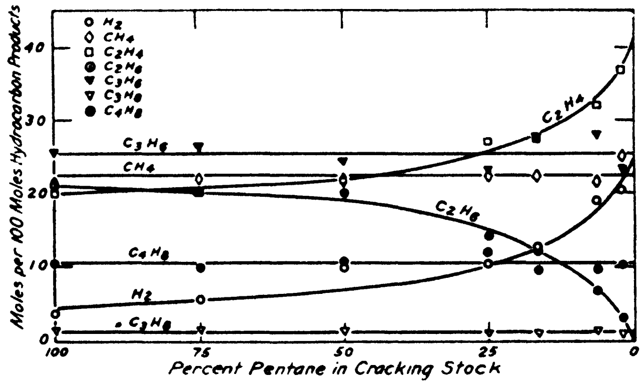
[80] G. Egloff, C. L. Thomas and C. B. Linn, *Ind. Eng. Chem.*, 1936, 28, 1283; *J. Inst. Pet. Tech.*, 1937, 23, 21A; *Chem. Abs.*, 1936, 30, 7988.

[81] H. Tropsch and G. Egloff, *Ind. Eng. Chem.*, 1935, 27, 1063; *J. Inst. Pet. Tech.*, 1935, 21, 408A; *Brit. Chem. Abs.* B, 1935, 1035; *Chem. Abs.*, 1935, 29, 7935.

It is interesting to note that equation (1) is entirely suppressed at contact times of more than 0.00203 second. The formation of ethylene is quite prominent, as will be seen from Fig. 17 showing the relation between yield and time of contact. From the graph, the maximum yields per 100 liters of isobutane charged with the corresponding contact times are: propene, 46 l. at 0.0035 second, ethylene, 44 l. at 0.0048 second, and acetylene, 35 l. at 0.0045 second.

PENTANES

The primary products obtained in the pyrolysis of the three isomeric pentanes are quite varied. Frey and Hepp[82] have studied the decomposition of these hydrocarbons at relatively low temperatures and pressures under conditions of limited dissociation. Their results are in direct conflict with the conclusions of Norris and Thomson[83] that at low temperatures rupture of the carbon chain can be made to take place at preferred points. Frey and Hepp have established the fact that the carbon-carbon bonds in all points in the molecule exhibit similar tendencies to break both in branched as well as normal chains. Under conditions of limited pyrolysis in cases where olefins capable of existence in several isomeric forms may be produced, the double bond remains the point of rupture. Naturally, isomerization of such olefins may occur under more exacting pyrolytic conditions, but the normal paraffins yielded only olefins under the comparatively mild conditions used by these investigators. Where olefins were produced by the scission of a side chain from isopentane and neopentane, the double bond at the point of rupture was located in the inner and not the terminal position.



Courtesy Industrial and Engineering Chemistry

FIG. 18.—Effect of Dilution on Decomposition of Pentane at 600°C. (J. J. Morgan and J. C. Munday)

n-Pentane. On the basis of the Rice mechanism,[84] the decomposition of n-pentane may be summed up as:

$$n\text{-}C_5H_{12} \longrightarrow 2C_2H_4 + CH_4$$
$$n\text{-}C_5H_{12} \longrightarrow C_3H_6 + C_2H_6 \text{ (or } C_2H_4 + H_2)$$
$$n\text{-}C_5H_{12} \longrightarrow C_4H_8 + CH_4$$

---

[82] F. E. Frey and H. J. Hepp, *Ind. Eng. Chem.*, 1933, **25**, 441; *Brit. Chem. Abs.* B, 1933, 581; *Chem. Abs.*, 1933, **27**, 2670.

[83] J. F. Norris and G. Thomson, *J.A.C.S.*, 1931, **53**, 3108; *Chem. Abs.*, 1931, **25**, 4842; *Brit. Chem. Abs.* A, 1931, 1147.

[84] F. O. Rice, *J.A.C.S.*, 1931, **53**, 1959; *Chem. Abs.*, 1931, **25**, 2967; *Brit. Chem. Abs.* A, 1931, 819. See also F. O. and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, 1935.

In agreement with these predictions, Frey and Hepp[85] find that the primary products at limited dissociation in the range of 396° to 560°C. are hydrogen, methane, ethylene, ethane, propene, 1-butene and pentenes, with only small amounts of other products.

Morgan and Munday[86] investigated the decomposition of pentane at 600-800°C. Dilution of the hydrocarbon with steam shows that the rate of dissociation is independent of the concentration, which indicates that the primary decomposition is essentially of the first order. See Table 15. The results are in accord with the Rice mechanism but do not agree with that proposed by Kassel.[87] The formation of propane is explained by the equation:

$$C_5H_{12} \longrightarrow C_3H_8 + C_2H_4$$

TABLE 15.—*Decomposition of* n-*Pentane.*

Temperature, °C.	600	600	600	600	600	600	600	650	700	750	800
Composition of cracking stock, %											
Pentane	100	75	50	25	16.7	6.3	2	100	100	100	16.7
Steam	0	25	50	75	83.3	93.7	98	0	0	0	83.3
Analysis,[a] mole %											
H_2	5.6	5.3	9.3	9.4	11.4	16.1	16.8	5.8	7.3	10.6	18.9
CH_4	20.8	20.8	20.0	20.3	19.8	18.1	20.7	23.5	29.7	36.4	44.1
C_2H_4[b]	19.3	19.1	19.7	24.6	24.2	27.2	30.6	22.8	27.4	31.5	35.0
C_2H_6	19.8	19.3	18.1	13.0	10.7	5.7	2.7	16.4	10.6	8.9	1.6
C_3H_6	22.8	24.8	22.2	21.0	24.5	23.7	19.4	23.6	20.3	10.5	0.3
C_3H_8	1.3	1.2	1.1	0.7	0.9	1.1	1.0	0.8	0.5	0.4	0.1
C_4H_8[c]	10.4	9.4	9.2	10.9	8.4	8.0	8.8	7.0	4.2	1.7	0.0
C_4H_{10}	—	0.1	0.4	0.1	0.1	0.1	—	0.1	—	—	—

[a] Does not include small amounts of liquid boiling higher than pentane and formed above 700°C.
[b] Includes some acetylene at 700°C. and above.
[c] Includes some 1,3-butadiene at 700°C. and above.

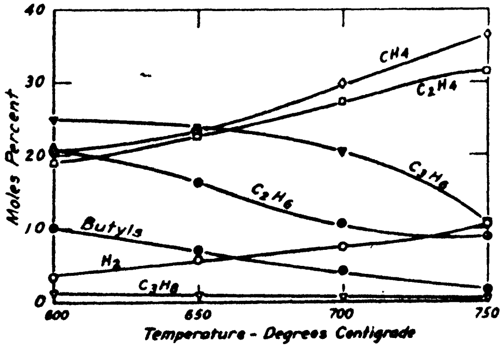


FIG. 19.
Thermal Decomposition of Pentane at Atmospheric Pressure. (J. J. Morgan and J. C. Munday)

Courtesy Industrial and Engineering Chemistry

Fig. 18 shows the effect of pressure on pyrolysis of pentane at 600°C. Increased dilution increases the formation of ethylene and hydrogen at the expense of the ethane, which is perfectly explicable in terms of the Rice theory. The effect of increased temperature can be readily ascertained from Fig. 19.

Isopentane. Isopentane which contains primary, secondary and tertiary carbon atoms may be expected to undergo decomposition with rupture of the carbon chain at all of the available positions. Thus, in accordance with the Rice mechanism, demethylation to 2-butene and isobutene, de-ethylation to propene, de-ethylenation to propane and dehydrogenation to pentenes may be expected.[88] Products obtained at 398-575°C. by Frey and Hepp[89] substantiate these reactions.

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[85] F. E. Frey and H. J. Hepp, *loc. cit.*

[86] J. J. Morgan and J. C. Munday, *Ind. Eng. Chem.*, 1935, 27, 1082; *J. Inst. Pet. Tech.*, 1935, 21, 409A; *Brit. Chem. Abs.* A, 1935, 1348; *Chem. Abs.*, 1935, 29, 7269. J. C. Munday, Dissertation, Columbia University, New York City, 1934.

[87] L. S. Kassel, *J. Chem. Phys.*, 1933, 1, 749; *Chem. Abs.*, 1934, 28, 463; *Brit. Chem. Abs.* A, 1934, 54. This theory has been discussed briefly in the introduction to this chapter.

Neopentane (tetramethylmethane). According to Rice[90] the only chain reaction possible in the decomposition of this hydrocarbon should be one involving the formation of methane and isobutene. Again, Frey and Hepp[91] substantiate the Rice mechanism, at 575°C. the products being methane and isobutene together with traces of hydrogen and 1-butene.[92]

The data of Frey and Hepp on the three pentanes are listed in Table 16.

TABLE 16.—*Pyrolysis of Pentanes.*

	n-Pentane		*iso*-Pentane			Neopentane
Temperature, °C.	396	560	398	570	575	575
Pressure, mm.	510	74	560	76	77	400-600
Time of contact, sec.	14,800	27	14,400	16.1	12.2	95
Analysis of products, mole %						
H_2	0.04	1.58	0.03	1.23	1.37	0.3
CH_4	0.47	3.08	1.04	5.14	4.39	18.3
C_2H_4	0.18	3.05	0.16	1.80	1.49	—
C_2H_6	0.60	2.32	0.16	0.91	0.59	—
C_3H_6	0.55	3.54	0.23	2.36	1.87	—
C_3H_8	0.07	0.16	0.13	0.14	0.12	—
C_4H_6	—	0.08	—	0.23	—	—
$(CH_3)_2C{=}CH_2$	—	—	0.44	2.44	2.00	16.0
C_4H_8	0.23	1.86	0.25	1.70	1.71	<0.9
C_4H_{10}	0.05	0.12	0.33	0.44	0.12	—
C_5H_8	0.01	—	—	—	—	—
C_5H_{10}	0.30	0 39	0.36	0.25	0.17	—

n-HEXANE

The pyrolysis of *n*-hexane at normal pressure and at temperatures slightly above incipient decomposition (520°C.) has been carried out by Dintzes and Frost.[93] The results indicate four primary decomposition equations:

$$
\begin{aligned}
&(1)\quad n\text{-}C_6H_{14} \longrightarrow C_6H_{12} + H_2\\
&(2)\quad n\text{-}C_6H_{14} \longrightarrow C_5H_{10} + CH_4\\
&(3)\quad n\text{-}C_6H_{14} \longrightarrow C_4H_8 + C_2H_6\\
&(4)\quad n\text{-}C_6H_{14} \longrightarrow C_3H_6 + C_3H_8
\end{aligned}
$$

which are always accompanied by secondary reactions,

$$
\begin{aligned}
&(5)\quad C_6H_{12} \longrightarrow C_4H_8 + C_2H_4\\
&(6)\quad C_6H_{12} \longrightarrow 2C_3H_6\\
&(7)\quad C_5H_{10} \longrightarrow C_3H_6 + C_2H_4\\
&(8)\quad C_4H_8 \longrightarrow 2C_2H_4
\end{aligned}
$$

The latter equations are greatly affected by the temperature and the time of contact.

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[88] F. O. Rice and M. D. Dooley, *J.A.C.S.*, 1933, 55, 4245; *Brit. Chem. Abs.* A, 1933, 1269; *Chem. Abs.*, 1933, 27, 5713.

[89] F. E. Frey and H. J. Hepp, *loc. cit.*

[90] F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, 1935.

[91] F. E. Frey and H. J. Hepp, *loc. cit.*

[92] See also C. D. Hurd, "The Pyrolysis of Carbon Compounds." The Chemical Catalog Co., Inc., New York, 1929, 22.

[93] A. I. Dintzes and A. V. Frost, *J. Gen. Chem., (U.S.S.R.)*, 1933, 3, 747; *Chem. Abs.*, 1934, 28, 2598; *Brit. Chem. Abs.* A, 1934, 151. A. I. Dintzes, *Compt. rend. acad. sci. U.R.S.S.*, 1933, 4, 153; *Brit. Chem. Abs.* A, 1934, 259; *Chem. Abs.*, 1934, 28, 2169. *Foreign Petroleum Tech.*, 1934, 2 (3), 81; *J. Inst. Pet. Tech.*, 1934, 20, 404A.

In these experiments, the hydrocarbon was heated almost to the cracking temperature and then passed through copper-lined iron tubes immersed in a metal bath. At 525° to 565°C. and a contact time of 6.1 to 90.8 seconds, a 3 to 8 per cent dissociation was obtained. Hexane decomposes mainly according to reactions (2) and (3) and only slightly following (1) and (4). Secondary decompositions proceed to the extent of 40 to 60 per cent. Over this temperature range the energy of primary decomposition is given as 64.5±1.5 kg.-cal. per mole and the velocity constant as

$$\log_{10}k = 14.22 - \frac{14{,}105}{T} \pm 0.031$$

These investigations were furthered by Dintzes and Zherko[94] to include more profound decomposition. At 588°C. with a contact time of 20 to 200 seconds, 27 to 60 per cent dissociation was observed. From the decomposition velocity constants calculated according to both first- and second-order equations, it was demonstrated that the cracking relations of this hydrocarbon and also of octane under the same conditions cannot be described by the classical equations of chemical kinetics. For a first-order process, the velocity constant falls off sharply with increase in per cent of decomposition from 10 to 60. This may be attributed to the retarding action of some of the reaction products. The equation,

$$kt = \left[\ln \frac{1}{1-x}\right] - \beta x$$

is adapted to the decomposition.

The theory that the retardation is caused by inactivation of free radicals formed early in the decomposition by their recombination is not accepted by Dintzes and Zherko. Their conclusion is that the free radicals react with the products already formed to yield a complex which is not broken up in collision with a new molecule. The original hydrocarbon is decomposed unimolecularly by heat into radicals by rupture of the carbon bonds. These radicals in turn are transformed into olefins and simpler radicals, such as methyl and ethyl, which react with molecules of the original hydrocarbons, detaching hydrogen atoms and forming the corresponding complex radicals which decompose anew into olefins and simpler radicals. The interaction of the radicals with the original hydrocarbon accounts for the rapid increase in reaction velocity at the start of the decomposition, which period is of relatively short duration. At the same time the radicals begin to become inactivated by the interaction with other products. The result of these two simultaneous processes is that the reaction velocity passes through a maximum and then gradually diminishes.

As a result of their studies on *n*-hexane and *n*-octane, Moldavskii, Kobuil'skaya and Livshitz[95] concluded that thermal isomerization of hydrocarbons is brought about chiefly as the result of secondary decompositions of the reaction products and not by rearrangement of the hydrocarbon skeleton. This was based on the observation that heat treatment at atmospheric pressure and temperatures up to about 600°C. produced practically no isomerization or change of the hydrocarbons. However, the factors that increased the degree of cracking (i.e., time, temperature and catalytic action of iron chamber walls) also increased the isomerization.

Griffith[96] found that the decomposition of hexane at 500°C. is greatly influenced by the addition of silica to a molybdenum oxide catalyst. The maximum effect is reached at a concentration of 4 moles of promoter to 100 of catalyst. The same ratio holds when the oxides of sodium, chromium, cerium, aluminum, boron, barium and thallium are used as promoters, but it is one-half as high with easily reducible oxides such as those of lead, iron or copper.

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[94] A. I. Dintzes and A. V. Zherko, *J. Gen. Chem. (U.S.S.R.)*, 1936, 6, 68; *Chem. Abs.*, 1936, 30, 4745; *Brit. Chem. Abs.* A, 1936, 939.

[95] B. L. Moldavskii, M. V. Kobuil'skaya and S. E. Livshitz, *J. Gen. Chem. (U.S.S.R.)*, 1936, 6, 616; *Chem. Abs.*, 1936, 30, 5555; *Brit. Chem. Abs.* A, 1936, 960.

[96] R. H. Griffith, *Nature*, 1936, 137, 538; *Chem. Abs.*, 1936, 30, 3706. Also R. H. Griffith and J. H. G. Plant, *Proc. Roy. Soc.*, 1935, A148, 186; *Chem. Abs.*, 1935, 29, 2335.

Pearce and Newsome[97] have studied the effect of pressures of about 1000 atmospheres at temperatures between 430° and 520°C. at heating times varying from a few minutes to 2 hours. In the interval 460-490°C., the production of gaseous paraffins predominates, methane, ethane, propane and butane being formed in percentages of 25, 47, 15 and 7, respectively. The amount of gaseous olefins produced is very small and tends to diminish with rise in temperature. At 497°C. an abundant carbonization begins and the proportion of methane is noticeably increased and continues to do so with higher temperatures. Liquid hydrocarbons, including cycloparaffins, benzene, substituted benzenes and higher olefins are also obtained.

At 670° to 750°C., under atmospheric pressure, decomposition is essentially in accordance with the equation,[98]

$$C_6H_{14} \longrightarrow CH_4 + C_2H_4 + C_3H_6$$

The formation of tar and coke, which are produced in small amounts, was inhibited by the dilution of the hydrocarbon with steam.

HIGHER PARAFFIN HYDROCARBONS

Experimental data on the pyrolysis of higher paraffin hydrocarbons are apparently not available. The primary decomposition of these hydrocarbons is best represented by a series of equations indicating the rupture of the carbon chain at any position with the formation of an olefin and the complementary lower paraffin, or, at the limit, hydrogen. This rule, though not entirely self-sufficient, satisfactorily represents the chief mode of decomposition. A more complete picture is furnished by the theory of free radicals. On the assumption that methyl, ethyl, isopropyl and *ter*-butyl radicals are stable and that the relative chances of loss of primary, secondary and tertiary hydrogen atoms can be expressed quantitatively by the ratio 1:2:10 at 600°C., Rice[99] has calculated the proportions of various hydrocarbons to be expected in the primary decomposition of certain higher paraffins. The results of this calculation are shown in Table 17.

Heptane. Matignon and Seon[100] find that the pyrolysis of heptane at 700°C. in a quartz tube at atmospheric pressure furnishes large quantities of higher olefins but only small amounts of ethylene. Dilution of the hydrocarbon with steam increases the formation of ethylene at the expense of the higher homologues. At 935°C. with about 80 per cent dilution, the yield of ethylene is 76 per cent.[101]

It is interesting to note that *n*-heptane is isomerized to the extent of 20-25 per

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[97] J. N. Pearce and J. W. Newsome, *Proc. Iowa Acad. Sci.*, 1934, **41**, 139; *Chem. Abs.*, 1935, **29**, 3649; *Brit. Chem. Abs.* **A**, 1936, 51.

[98] E. Terres, C. Walther, H. Schmidt, J. Pomeraniec and O. Focsaner, *Öl. u. Kohle*, 1934, **2**, 2, 56; *Chem. Abs.*, 1935, **29**, 6743; *Brit. Chem. Abs.* **B**, 1935, 391.

[99] F. O. Rice, *Ind. Eng. Chem.*, 1934, **26**, 259; *Brit. Chem. Abs.* **B**, 1934, 486; *Chem. Abs.*, 1934, **28**, 6990.

[100] C. Matignon and M. Seon, *Compt. rend.*, 1934, **198**, 1649; *Brit. Chem. Abs.* **A**, 1934, 752; *Chem. Abs.*, 1934, **28**, 5037.

[101] F. O. Rice and O. L. Polly (*Ind. Eng. Chem.*, 1935, **27**, 915; *Brit. Chem. Abs.* **A**, 1935, 1229; *Chem. Abs.*, 1935, **29**, 6578) obtained cyclohexane, *n*-heptane and tetradecane in the pyrolysis of di-*n*-heptyl mercury. The formation of the cyclohexane is attributed to the direct decomposition of the free heptyl radical, and not to polymerization of ethylene. F. O. Rice (British P. 407,036, 1934; *Chem. Abs.*, 1934, **28**, 4847; *Brit. Chem. Abs.* **B**, 1934, 444; *J. Inst. Pet. Tech.*, 1934, **20**, 332A) has suggested a method of preparing organo-lead compounds, namely by heating the hydrocarbons to 800-1000°C. at reduced pressure in the absence of air and passing the vapors over finely divided lead. The reaction mixture is cooled to low temperatures to separate the lead alkyls.

TABLE 17.—*Products Formed in Moles per Mole of Hydrocarbon Decomposed at 600°C. and under Pressure.*

Hydrocarbon	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	*n*-C_4H_8	*sec*-C_4H_8	*iso*-C_4H_8	*iso*-C_4H_{10}	Higher Olefin
n-Hexane	0.546	0.91	0.455	0.364	—	0.182	—	—	—	0.182
3-Methylpentane	0.74	0.223	0.26	0.223	—	0.111	0.148	—	—	0.52
2,3-Dimethylbutane	0.81	—	—	0.188	0.188	—	—	—	—	0.81
n-Heptane	0.54	1.17	0.463	0.308	—	0.154	—	—	—	0.308
2,4-Dimethylpentane	0.445	—	—	0.334	0.056	—	—	0.556	—	0.278
2,2,3-Trimethylbutane	0.7	—	—	0.12	0.18	—	—	0.18	0.18	0.7
n-Octane	0.534	1.4	0.467	0.267	—	0.133	—	—	—	0.4
2,5-Dimethylhexane	0.75	0.15	—	0.15	0.75	—	—	0.5	—	0.35
2,2,4-Trimethylpentane	0.656	—	—	0.259	—	—	—	0.605	0.346	0.397
n-Nonane	0.53	1.65	0.471	0.236	0.118	—	—	—	—	0.471
2,6-Dimethylheptane	0.455	0.591	—	0.364	0.546	—	—	0.455	—	0.41
n-Decane	0.528	1.9	0.474	0.211	—	0.105	—	—	—	0.526
2,2,6-Trimethylhexane	0.5	0.347	—	—	—	—	—	0.347	0.5	0.654

cent by heating with zinc chloride at 300° to 400°C. for 6 hours.[102] Molybdenum sulphide at 410-420°C. causes considerable rearrangement in both *n*-heptane and *n*-octane, and at slightly higher temperatures (440°C.) the latter hydrocarbon also undergoes considerable cracking in addition to isomerization.

Octanes. According to Dintzes,[103] pyrolysis of *n*-octane and of 2,5-dimethyl hexane follows the reactions:

$$(1)\ C_8H_{18} \longrightarrow C_7H_{14} + CH_4 \qquad (3)\ C_8H_{18} \longrightarrow C_5H_{10} + C_3H_8$$

$$(2)\ C_8H_{18} \longrightarrow C_6H_{12} + C_2H_6 \qquad (4)\ C_8H_{18} \longrightarrow C_8H_{16} + H_2$$

In a copper-lined iron tube at 496-570°C. at normal pressure and with contact times of 6 to 130 seconds, equation (1) accounts for about 80 to 90 per cent of the total *n*-octane decomposed. Secondary reactions involving decomposition of the various olefins proceed to the extent of 60 to 70 per cent. Over this temperature range the energy of activation of *n*-octane is 64.5 kg.-cal. per mole and the primary dissociation constant is given by

$$\log_{10}k = 14.70 - \frac{14{,}100}{T} \pm 0.09$$

At 570°C. with contact times of 4 to 215 seconds, *n*-octane undergoes 5.7 to 61 per cent dissociation.[104]

2,5-Dimethylhexane, at 492-576°C. for 3 to 38 seconds, decomposes to the extent of 75 to 80 per cent according to equation (1), and the olefins undergo 50-70 per cent secondary decomposition.[105] The activation energy for the primary dissociation is related to the temperature by the equation:

$$\log_{10}k = 6.553 - \frac{7215}{T} \pm 0.05$$

Nonane. The pyrolysis of *n*-nonane at 670-750°C. results chiefly in the formation of pentene and butene, octene and methane, and hexene and ethane.[106] The primary reactions are further complicated by secondary olefin decomposition, as noted with the other normal paraffins cited.

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[102] A. D. Petrov, A. P. Meshcheriakov and D. N. Andreev, *Ber.*, 1935, 68, 1; *Chem. Abs.*, 1935, 29, 2145, *Brit. Chem. Abs.* A, 1935, 324.

[103] A. I. Dintzes, *Compt rend. acad. sci. U.R.S.S.*, 1933, 4, 153; *Chem. Abs.*, 1934, 28, 2169; *Brit. Chem. Abs.* A, 1934, 259.

[104] A. I. Dintzes and A. V. Zherko, *J. Gen. Chem. (U.S.S.R.)*, 1936, 6, 68; *Chem. Abs.*, 1936, 30, 4745; *Brit. Chem. Abs.* A, 1936, 939.

[105] A. I. Dintzes, *loc. cit.* A. I. Dintzes and A. V. Frost, *J. Gen. Chem. (U.S.S.R.)*, 1934, 4, 610; *Brit. Chem. Abs.*, A, 1934, 1311; *Chem. Abs.*, 1935, 29, 2058, 4244.

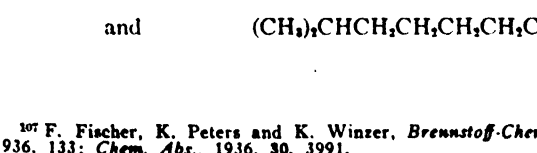
[106] E. Terres, C. Walther, H. Schmidt, J. Pomeraniec and O. Focsaner, *Oel. u. Kohle*, 1934, 2, 2, 53; *Chem. Abs.*, 1935, 29, 6743; *Brit. Chem. Abs.* B, 1935, 391.

Higher Paraffins. Fischer, Peters and Winzer[107] decomposed Kogasin II (the higher boiling fraction of the liquid hydrocarbon mixture obtained by the Fischer-Tropsch process[108]) by immersing an electrically heated wire into the liquid. The products consisted of 20 per cent of a highly unsaturated light oil and 80 per cent of gaseous hydrocarbons, principally ethylene and its homologues. Other Kogasin fractions treated in this manner lead to similar results.

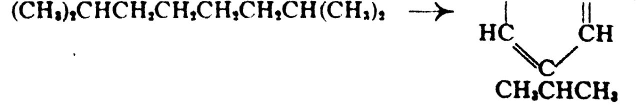
Under high pressure (110 to 265 atmospheres) of hydrogen, at 440°C. octadecane undergoes 88.5 per cent decomposition[109] yielding a continuous series of liquid products from pentane to heptadecane, the amounts of which decrease with increase of molecular weight. About 7 to 8 per cent of unsaturated compounds, small quantities of naphthenes and traces of benzene were obtained. The molecular yield[110] was 303 per cent, indicating that on the average each molecule was split twice. Gorniak and Szayna have obtained similar products with paraffin wax. At 440°C. the latter underwent 96.5 per cent decomposition with a molecular yield of 393 per cent, while at 446°C. the corresponding values were 98.6 and 465 per cent. With a rise in temperature the series of products contains an increased proportion of materials of low molecular weight at the expense of those of high molecular weight.

Catalytic Cyclization of Aliphatic Hydrocarbons

Moldavskii and Kamusher[111] report that when aliphatic hydrocarbons containing 6 or more carbon atoms are heated to 460-470°C. and passed over chromic oxide, they are readily transformed into members of the benzene series. Thus, *n*-hexane at 460°C., by undergoing ring formation and simultaneous dehydrogenation gave 17 per cent of benzene. At 470°C., *n*-heptane was converted into toluene (26 per cent). In the case of *n*-octane, however, at 460°C. the transformation followed two courses, resulting in the production of *o*-xylene (63 per cent) and small amounts of ethylbenzene. 2,5-Dimethylhexane and 2,7-dimethyloctane followed an analogous cyclization-dehydrogenation reaction, being converted into *p*-xylene (36 per cent) and *m*-methylisopropyl benzene (82 per cent), respectively, according to the equations:



and



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[107] F. Fischer, K. Peters and K. Winzer, *Brennstoff-Chem.*, 1935, 16, 421; *Brit. Chem. Abs.* B, 1936, 133; *Chem. Abs.*, 1936, 30, 3991.

[108] This involves interaction of carbon monoxide and hydrogen. See Chapter 52.

[109] J. Gorniak and A. Szayna, *Przemysl Chem.*, 1934, 18, 57; *Chem. Abs.*, 1934, 28, 4876; *Brit. Chem. Abs.* B, 1934, 442.

[110] By molecular yield is meant the number of molecules obtained in reaction. Thus in this case, one molecule gave rise to 3.03 molecules, or on a percentage basis, 303 moles of products per 100 moles of octadecane reacting.

[111] B. L. Moldavskii and H. Kamusher, *Compt. rend acad. sci., U.R.S.S.*, 1936, 1, 355; *Chem. Abs.*, 1936, 30, 6713; *Brit. Chem. Abs.* A, 1936, 818; *Chem. Zentr.*, 1936, 1, 2339.

Octane and butylbenzene underwent similar changes, the former giving rise to *o*-xylene and the latter to naphthalene. The presence of olefins in the reaction mixture was also noted. This was attributed to the simultaneous dehydrogenation of the paraffins. Cyclization of a gasoline fraction was also attempted, but the reaction was found to be greatly complicated by the dehydrogenation of naphthenic hydrocarbons. Moldavskii and Kamusher also investigated the use of zinc oxide, alumina, nickel chromate, and uranium oxide and fluoride, and report that all of these were without catalytic activity. Molybdenum sulphide, however, acts similar to chromic oxide, but becomes deactivated much more rapidly than the latter.

MONOLEFIN HYDROCARBONS

Three main types of reaction can be discerned in the pyrolysis of monolefin hydrocarbons under conditions of limited decomposition, namely:

(1) Dissociation into hydrocarbons of lower molecular weight and hydrogen (true pyrolysis).
(2) Isomerization.
(3) Polymerization to yield hydrocarbons of higher molecular weight.

To emphasize the greater complexity encountered in the decomposition of unsaturated compounds compared with the corresponding saturated hydrocarbons, it should be remembered that paraffins undergo only the first two of these three transformations; the higher-boiling polymeric products are not generated from the latter except as secondary effects.[112] Paraffins do not show polymerization reactions because the temperatures for their decomposition to olefins are higher than those at which polymerization occurs.[113]

Frolich[114] has pointed out how exceedingly complicated the pyrolysis of a simple hydrocarbon such as propene may become because of secondary decompositions. It is practically impossible to include the reactions which the unsaturated constituents of all these secondary products may subsequently undergo, but the entire series of the primary compounds, most of which have been actually identified, can be explained on the basis of the Rice free-radical mechanism.[115] This reasoning explains why so many of the reactions appear to be non-reversible: although written as bimolecular for simplicity, in the light of the free radical changes involved they really become monomolecular. The fact that free radical collision is such an important factor helps to explain why diminished pressure and an equivalent dilution with inert material give such widely different results insofar as the product-consumption is concerned. Probability calculations will undoubtedly prove an aid to substantiate or disprove some of the reactions advanced.

Such variables as temperature, pressure, time of contact and catalysts seem to have a more profound influence on polymerization than on cracking. It may be possible, by proper choice of conditions, to favor the formation of one or more of the cracking products at the expense of the others, but the basic decomposition reactions remain more or less unaltered, according to Frolich.[116] In the case of polymerization the course of the reactions (and therefore the products formed) may be entirely governed by the operating conditions. Low-temperature catalytic treatment gives primarily an olefin with some degree of branchiness. Increase in both temperature and pressure causes a growing tendency for ring closure with the corresponding formation of naphthenic structures. Increase in temperature alone permits additional hydrogen to split off with simultaneous ring formation, yielding aromatic type products. Although analytical methods are not so well developed that it is possible to identify all of the polymerization compounds and account for the composition of the entire product, certain typical substances can be isolated in sufficient quantities to substantiate his general conclusion.

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[112] C. D. Hurd, *Ind. Eng. Chem.*, 1934, **26**, 50; *Brit. Chem. Abs.* **B**, 1934, 228; *Chem. Abs.*, 1934, **28**, 1014.

[113] G. Egloff and E. Wilson, *Ind. Eng. Chem.*, 1935, **27**, 917; *J. Inst. Pet. Tech.*, 1935, **21**, 369A; *Brit. Chem. Abs.* **A**, 1935, 1206; *Chem. Abs.*, 1935, **29**, 6203.

[114] P. K. Frolich, private communication; citation from unpublished paper presented to Society of Chemical Industry, N. Y. Section, Apr. 3, 1936. See also V. Schneider and P. K. Frolich, *Ind. Eng. Chem.*, 1931, **23**, 1405; *Chem. Abs.*, 1932, **26**, 1257; *Brit. Chem. Abs.* **A**, 1932, 27. P. K. Frolich and P. J. Wiezevich, *Ind Eng. Chem.*, 1935, **27**, 917; *Brit. Chem. Abs.* **B**, 1935, 980; *J. Inst. Pet. Tech.*, 1935, **21**, 408A; *Chem. Abs.*, 1935, **29**, 7624.

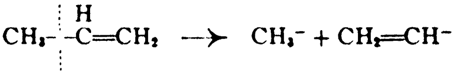
[115] See F. O. Rice and K. K. Rice ("The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, 1935, Chapter 8) for a discussion of this theory.

[116] P. K. Frolich, *loc. cit.*

The more probable reactions in the decomposition of propene have been outlined by Frolich. Simple dehydrogenation gives propadiene:

$$(1)\ C_3H_6 \longrightarrow C_3H_4 + H_2$$

Scission of the carbon-carbon bond would result in the formation of methyl and vinyl radicals, as



$$CH_3-\vdots-\overset{H}{C}{=}CH_2 \longrightarrow CH_3^- + CH_2{=}CH^-$$

Either of these radicals may be expected to have a strong tendency to saturate itself by removing a hydrogen atom from the other. On transfer of 1 hydrogen to the vinyl radical, ethylene is formed, while at the same time the methylene residue may attach itself to a propene molecule, giving butene:

$$CH_2^- + C_3H_6 \longrightarrow C_4H_8$$

with an over all effect:

$$(2)\ 2C_3H_6 \longrightarrow C_2H_4 + C_4H_8$$

On the other hand, if the methyl radical succeeds in capturing a hydrogen atom, methane and acetylene become the products:

$$(3)\ C_3H_6 \longrightarrow CH_4 + C_2H_2$$

However, acetylene is extremely unstable so that Frolich believes it reasonable to assume that the primary acetylene residue will strive to combine with a molecule of propene with the formation of pentadiene:

$$\begin{aligned} C_2H_2^- + C_3H_6 &\longrightarrow C_5H_8 \\ \text{or}\ (4)\ 2C_3H_6 &\longrightarrow CH_4 + C_5H_8 \end{aligned}$$

which is evidently quite a prominent reaction. Still another possibility is for the primary radicals to react with themselves to give ethane and butadiene:

$$\begin{aligned} 2CH_3^- &\longrightarrow C_2H_6 \\ \text{and}\ 2C_2H_3^- &\longrightarrow C_4H_6 \end{aligned}$$

or an over all effect:

$$(5)\ 2C_3H_6 \longrightarrow C_2H_6 + C_4H_6$$

If scission of the double bond occurs, a different pair of radicals result:

$$CH_3CH{=}\vdots CH_2 \longrightarrow CH_3CH^- + CH_2^-$$

which might react with propene to form butene and pentene as:

$$(6)\ 3C_3H_6 \longrightarrow C_4H_8 + C_5H_{10}$$

Finally, polymerization of propene would explain the presence of hexene:

$$(7)\ 2C_3H_6 \longrightarrow$$

Unfortunately, the necessary experimental data to substantiate all of these reactions is lacking. However, Frolich has applied this method of reasoning to the results obtained by Schneider and Frolich[117] in the decomposition of propene at 725°C. and 0.2 atmosphere, as is shown in Table 18.

TABLE 18.—*Decomposition Products of Propene at 725°C. and 0.2 Atmosphere.*

Reaction	Product	Mole % Propene Reacting Determined	Mole % Propene Reacting Average
(1) $C_3H_6 \longrightarrow C_3H_4 + H_2$	C_3H_4	4[a]	5
	H_2	6	
(2) $2C_3H_6 \longrightarrow C_2H_4 + C_4H_8$	C_2H_4	46	46
	C_4H_8	46	
(3) $C_3H_6 \longrightarrow CH_4 + C_2H_2$	CH_4	5	5
	C_2H_2	5[a]	
(4) $2C_3H_6 \longrightarrow CH_4 + C_5H_8$	CH_4	16[b]	16
	C_5H_8	16	
(5) $2C_3H_6 \longrightarrow C_2H_6 + C_4H_6$	C_2H_6	9	10
	C_4H_6	11	
(6) $3C_3H_6 \longrightarrow C_4H_8 + C_5H_{10}$	C_4H_8	3	3
	C_5H_{10}	3	
(7) $2C_3H_6 \longrightarrow C_6H_{12}$	C_6H_{12}	9[c]	9

[a] Roughly estimated.

[b] By difference between analysis for total CH_4 and that required to satisfy Reaction (3).

[c] By difference between analysis for total "C_5 and C_6 unsaturates" and that required to satisfy Reactions (4) and (6).

As to the relative stability of the olefins towards decomposition at 600 to 700°C., **Egloff** and Parrish[118] estimate them to be in the following descending order: ethylene, propene, isobutene, 2-butene, 1-butene, trimethylethylene, 2-pentene and 1-pentene.

Egloff and Wilson[119] state that the nature of the reaction products is dependent upon temperature, pressure and contact time. The energy of activation is an important guide to possible reactions at a given temperature, but there is no corresponding guide for the effects of pressure. The simple relation of a change in volume during a reaction measures only effects due to large variations in pressure. Although the latter greatly influence the nature of the substances formed, the exact relationships remain to be found. For a given temperature and pressure the contact time determines the actual products obtained.

Polymerization of an olefin to nonaromatic compounds occurs at the initial temperatures of reaction. The relative ability of a particular olefin to polymerize will depend on its structure. In general, points of unsaturation are conducive for this action, provided the unsaturated carbon atoms are not too highly substituted with methyl or ethyl groups.[120] Points of unsaturation also promote isomerization and since these particular reactions have low energies of activation, the most favorable conditions are low temperatures and long contact times.[121]

With respect to catalysts, it has been pointed out[121a] that the characteristic action of such substances on olefins is the formation of carbon and hydrogen. However, liquid products may be obtained when sodium, iron, cobalt, copper, nickel or Ascoloy is employed. Reduction in activity is observed when deposition of carbon on the contact agent occurs or when the latter forms stable compounds with the hydrocarbons undergoing treatment. Of the alloys studied, Monel metal, Chromel (nickel and chromium) and Alumel (nickel, iron and silicon) promoted decomposition of the olefins into carbon and hydrogen.

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[117] V. Schneider and P. K. Frolich, *loc. cit.*

[118] G. Egloff and C. I. Parrish, *Chem. Rev.*, 1936, 19, 145; *Chem. Abs.*, 1937, 31, 94; *J. Inst. Pet. Tech.*, 1937, 23, 22A.

[119] G. Egloff and E. Wilson, *loc. cit.*

[120] See Chapter 26 for a discussion of polymerization.

[121] G. Egloff and E. Wilson, *loc. cit.*

[121a] G. Egloff and C. I. Parrish, *J.S.C.I.*, 1937, 56, 321.

ETHYLENE

Egloff and Wilson conclude that ethylene may be regarded as the basic hydrocarbon in thermal reaction. The key to the decomposition of most hydrocarbons can be found in a study of ethylene since the latter is an important product below 750°C. and above this temperature the resultants are essentially all derived from it. This olefin undergoes five main types of transformation, (1) polymerization, (2) hydrogenation to ethane, (3) scission of one carbon-hydrogen bond, (4) scission of the double bond and (5) dehydrogenation to acetylene, and these are shown in Fig. 20. The principal products obtained at normal pressure[122] and the approximate temperature ranges for their initial appearance and maximum formation are listed in Table 19.

TABLE 19.—*Pyrolytic Products of Ethylene.*

Product	Temperature, °C. Initial Formation	Temperature, °C. Maximum Formation
Butane, butenes	350-400	650-750
Ethane	450-500	700
Methane	500	1000
Acetylene	650-700	1400
Aromatics	650	800-850

Hurd and Eilers[123] have investigated the effect of various tube surfaces on the decomposition of ethylene in the range of 550-800°C. Ascoloy (a steel containing 24-30 per cent of chromium), quartz and Pyrex tubes were found to be noncatalytic, while iron effected considerable carbonization. See Table 20.

TABLE 20.—*Pyrolysis of Ethylene in Various Tubes.*

	Quartz	Glass	Ascoloy		Iron	
Temperature, °C.	575	650	775	802	550	550
Contact time, sec.	240	350-450	11	10.6	5.8	11.8
Extent of decomposition, %	16	24	30	54	10.6	26.7
Carbon formed, % total charged	—	—	—	—	10	22 5
Analysis of exit gas, volume %						
Acetylene	Trace	3.9	0.31	0.43	—	—
Isobutene	—	—	1.99	1.74	0.7	0.3
Propene	5.9	—	6.88	4.67	0.5	0.4
Ethylene	88.0	83.5	75.8	55.8	82.9	65.0
Hydrogen	—	3.1	3.76	13.1	14.6	33.1
Methane	2.7	4 2	5.96	6.4	0.0	0.0
Ethane	3.3	2.9	1.88	14.8	0.0	0.0

Pyrolysis at 700°C. for 1.5 to 6 minutes yields aromatic hydrocarbons almost exclusively, except for traces of unsaturated gases, according to Dubois.[124] Benzene, toluene, xylene, naphthalene and anthracene were identified in the tar obtained. Liquid hydrocarbons may also be produced by heating ethylene to 400-

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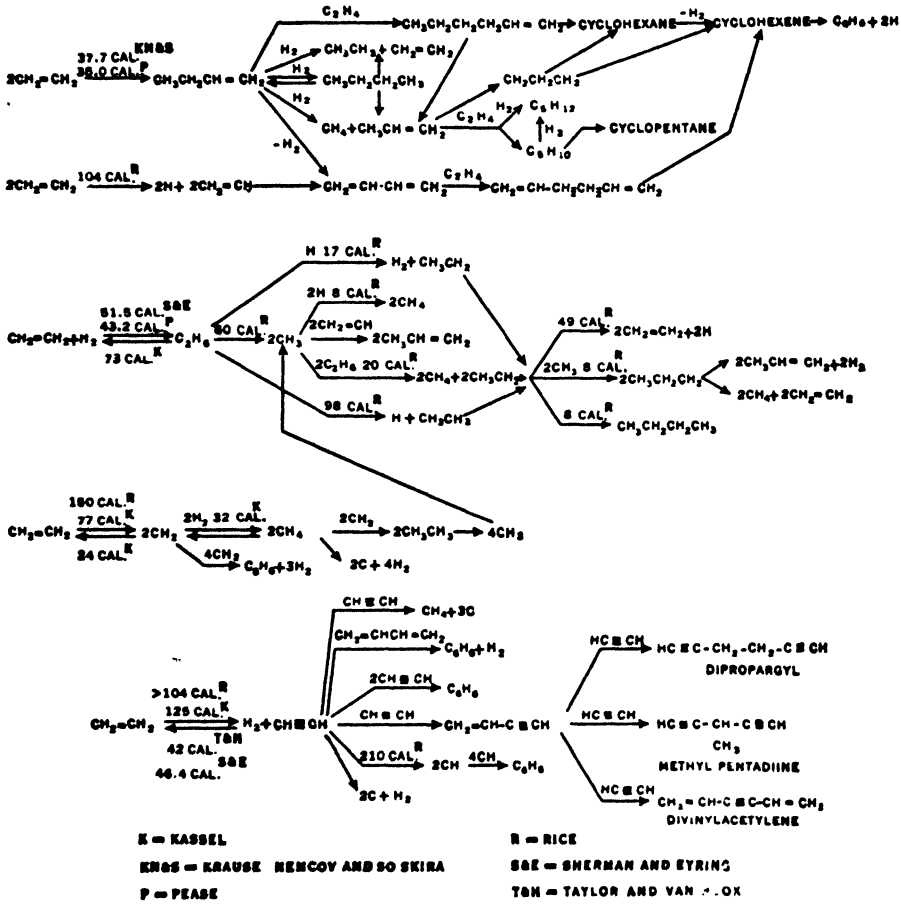
[122] H. I. Waterman (*Chem. Weekblad*, 1934, 31, 713; *Brit. Chem. Abs.* B, 1935, 835; *Chem. Abs.*, 1935, **29**, 3162) has reported that for some unkown reason, ethylene heated to 250°C. at 175 kg. per sq. cm. pressure, exploded, producing carbon, hydrogen and a little methane.

[123] C. D. Hurd and L. K. Eilers, *Ind. Eng. Chem.*, 1934, **26**, 776; *J. Inst. Pet. Tech.*, 1934, **20**, 493A; *Brit. Chem. Abs.* B, 1934, 792; *Chem. Abs.*, 1934, **28**, 5646.

[124] J. Dubois, *Przemysl Chem.*, 1933, 17, 188; *Chem. Abs.*, 1934, **28**, 7490.

1100°C. in the presence of 2 per cent of mercury or cadmium vapor.[125] A yield of 2 to 4 per cent of butadiene has been obtained at 700-750°C. by using a silica tube packed with copper gauze.[126] Five consecutive separations and recirculations of the gas lead to 9-10 per cent conversion to the diolefin along with some aromatic hydrocarbons. Greater rate of flow increased the formation of butadiene at the expense of the aromatics. Diminished pressure had no effect on the butadiene yield.



Courtesy Industrial and Engineering Chemistry

FIG. 20.—Thermal Reactions of Ethylene. (G. Egloff and E. Wilson)

High-temperature-low-pressure pyrolysis completely masks the primary reaction products because of intensive decomposition which occurs. Tropsch, Parrish and Egloff[127] studied the decomposition of ethylene at 1100° and 1400°C. under 50 mm.

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[125] F. Winkler and H. Haeuber, U. S. P. 1,986,238 and 1,986,239, Jan. 1, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1098.

[126] F. N. Voranov and A. V. Voranova, *Sintet. Kauchuk*, 1933(3), 5; *Chem. Abs.*, 1934, **28**, 3378; *Brit. Chem. Abs.* **B**, 1934, 819.

[127] H. Tropsch, C. I. Parrish and G. Egloff, *Ind. Eng. Chem.*, 1936, **28**, 581; *Brit. Chem. Abs.* **A**, 1936, 818; *J. Inst. Pet. Tech.*, 1936, **22**, 255A; *Chem. Abs.*, 1936, **30**, 4147.

pressure with very short contact times. At the lower temperature, acetylene and hydrogen are the principal products, together with smaller amounts of paraffins. Longer periods of contact favor higher yields, amounting to 21 and 48.4 per cent for acetylene and hydrogen, respectively, and 14.2 per cent for paraffins at 0.044 second. Formation of butadiene (about 1.5 per cent) and propene and butenes (3.0 per cent) is not greatly influenced by the contact time. At 1400°C., the results differ radically, in that no di- or monolefins (except ethylene) are found, the reaction being chiefly one of dehydrogenation to acetylene. Table 21 is a summary of the data obtained under these conditions.

TABLE 21.—*Pyrolysis of Ethylene at 50 mm. Pressure.*

Temperature, °C.	1100					1400				
Contact time, 10^{-3} sec.	0.7	2.2	6.1	14.0	44.0	0.8	1.6	2.3	4.1	8.4
Analysis, %										
C_2H_2	5.9	7.2	8.9	11.2	15.2	18.1	33.9	49.8	33.2	28.8
C_2H_4	88.5	77.5	61.5	48.5	35.1	47.9	14.0	11.3	6.0	6.1
$C_3H_6 + C_4H_8$	0.9	3.2	2.5	3.0	1.7	0.0	0.0	0.0	0.0	0.0
C_4H_6	1.4	0.6	1.3	1.2	0.6	—	—	—	—	—
H_2	0.2	4.7	17.5	24.1	34.6	28.0	45.9	29.4	52.6	54.0
C_nH_{2n+2}	2.8	2.2	5.8	9.4	10.2	4.6	4.5	7.2	4.0	5.3
n in Paraffins[a]	2.64	4.0	2.75	3.4	2.96	1.99	1.45	1.0	1.78	1.64
Yield, liters per 100 l. of ethylene charged										
C_2H_2	5.9	7.2	9.5	10.9	21.0	23.0	52.7	76.6	54.3	46.9
C_2H_4	88.0	77.0	65.8	61.0	48.0	60.8	21.8	17.4	9.8	9.9
$C_3H_6 + C_4H_8$	0.85	3.2	2.7	2.9	2.5	—	—	—	—	—
C_4H_6	1.4	0.6	1.4	1.4	0.8	—	—	—	—	—
H_2	0.2	4.7	18.2	31.0	48.4	35.6	71.5	45.2	86.4	88.2
C_nH_{2n+2}	2.8	2.2	6.2	7.1	14.2	5.9	7.0	11.1	6.6	8.6

[a] Average number of carbon atoms per molecule.

PROPENE

The two most probable types of decomposition for propene are (1) into hydrogen and an allyl radical and (2) into methyl and a vinyl radical. Rice[128] estimates the energy of activation for these two transformations to be 91,000 and 85,000 cal., respectively. Dissociation begins at 350°C., slightly lower than for ethylene, as might be expected from the asymmetry of the molecule. The thermal reactions of propene[129] are summarized in Fig. 21.

Travers[130] has shown that at 550°C. in the presence of hydrogen, decomposition is principally to ethylene and methane, while at the same time hexenes and pentenes are formed by the condensation of molecules of propene alone and with ethylene.

That the type of surface plays an important part in the pyrolysis of propene has been noted by Hurd and Eilers.[131] Monel metal is extremely destructive in its action, causing intense carbonization even at 350°C. Ascoloy (a chromium steel) is practically non-catalytic, and iron is intermediate between the two, as summarized in Table 22.

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[128] F. O. and K. K. Rice. "Aliphatic Free Radicals." The Johns Hopkins Press. Baltimore. 1935.

[129] G. Egloff and E. Wilson. *Ind. Eng. Chem.*, 1935. **27**. 917; *J. Inst. Pet. Tech.*, 1935. **21**. 369A; *Brit. Chem. Abs.* **A**, 1935. 1206; *Chem. Abs.*. 1935. **29**. 6203.

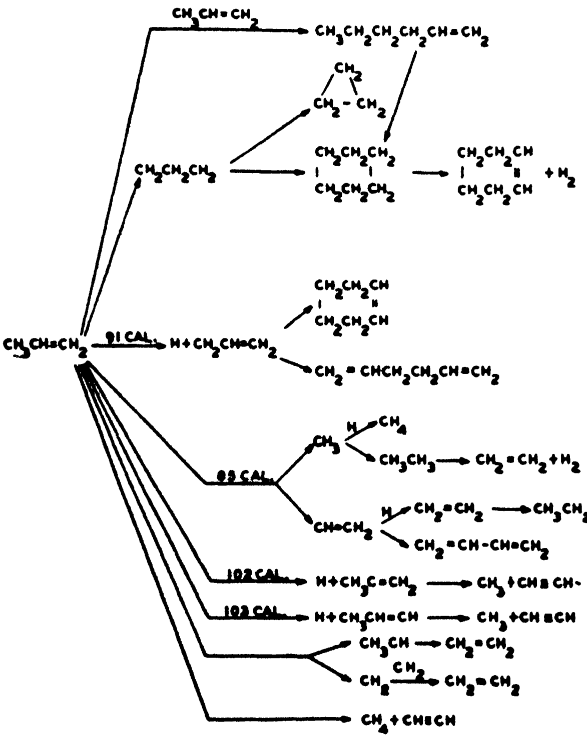
[130] M. W. Travers, *Trans. Faraday Soc.*, 1936, **32**, 236; *Chem. Abs.*, 1936, **30**, 2548; *Brit. Chem. Abs.* **A**, 1936. 309.

[131] C. D. Hurd and L. K. Eilers, *Ind. Eng. Chem.*, 1934, **26**, 776; *J. Inst. Pet. Tech.*, 1934, **20**, 493A; *Brit. Chem. Abs.* **B**, 1934, 792; *Chem. Abs.*, 1934, **28**, 5646.

TABLE 22.—*Pyrolysis of Propene in Various Tubes.*

	Glass		Ascoloy				Iron		Monel
Temperature, °C.	650	700	652	700	753	805	550	600	350
Contact time, sec.	30	25	7.1	7.0	7.7	7.3	27	21	25.8
Oil formation, % by weight of propene decomposed	—	27	—	—	12.3	37.2	0.0	0.0	0.0
Extent of decomposition	16	51	5	19	54	82	5.7	15.3	47.4
Carbonization, % total C charged	—	—	None	None	None	None	1.1	8.1	Much
Analysis of exit gases, volume %									
Acetylenes	0.9	1.8	—	0.31	0.44	0.43	—	—	—
Isobutene	2.1	2.1	1.23	1.87	1.78	1.95	—	—	0.5
Propene	82.0	43.0	96.1	83.3	47.6	16.0	96.8	83.5	37.6
Ethylene	4.9	17.7	1.64	8.21	20.7	29.0	0.9	2.4	0.3
Hydrogen	1.3	6.6	—	1.66	5.78	12.2	1.0	9.7	38.3
Paraffins	6.5	24.8	—	2.81	20.5	39.2	—	2.1	21.7
n in Paraffins[a]	1.3	1.2	—	1.86	1.53	1.14	—	2.54	1.81

[a] Average number of carbon atoms per molecule



Courtesy Industrial and Engineering Chemistry

FIG. 21.—Thermal Reactions of Propene. (G. Egloff and E. Wilson)

Observations of pyrolysis at 1100°C. and low pressures (50 mm.) in conjunction with short contact times show that lower paraffins (methane and ethane), ethylene, acetylene, hydrogen and small amounts of butadiene are formed.[132] At 1400°C. and the same pressure, propene is completely decomposed, hydrogen and acetylene resulting mainly. Butadiene is produced in small quantities but its formation is entirely suppressed at contact times greater than 0.0022 second. Data obtained in this investigation are summarized in Table 23.

TABLE 23.—*High-Temperature Pyrolysis of Propene at 50 mm. Pressure.*

Temperature, °C.	1100					1400				
Contact time, 10^{-3} sec....	2.2	2.5	4.3	5.8	12.0	0.9	1.2	1.6	3.0	3.8
Analysis, %										
C_2H_2..............	8.9	12.5	13.9	15.0	14.8	25.3	26.1	25.7	25.4	22.2
C_2H_4..............	10.5	13.1	17.1	18.9	19.4	14.0	10.3	7.8	4.1	2.1
$C_3H_6 + C_4H_8$	64.9	49.0	35.9	26.7	19.2	0.0	0.0	0.0	0.0	0.0
C_4H_6..............	0.7	1.8	2.0	2.2	1.9	2.2	1.4	1.0	0.0	0.0
H_2................	4.1	9.5	12.4	15.1	17.4	20.1	41.5	45.1	57.3	65.5
C_nH_{2n+2}............	8.8	13.9	17.7	20.5	25.7	36.7	19.3	18.6	11.6	8.0
n in Paraffin[a]........	1.39	1.27	1.07	1.23	2.03	1.41	2.23	1.6	1.35	1.06
Yield in liters per 100 l. of propene charged:										
C_2H_2....	9.9	14.7	17.2	19.3	21.8	47.8	54.5	54.2	56.4	56.0
C_2H_4.....	11.8	15.5	21.2	24.4	28.5	26.4	21.5	16.4	9.1	5.3
C_4H_6	0.8	2.1	2.5	2.8	2.9	4.2	2.9	2.1	0.0	0.0
H_2......	4.6	11.1	15.4	19.5	25.6	38.0	86.8	95.0	127.0	165.0
C_nH_{2n+2}..........	9.9	16.4	21.9	26.4	37.8	69.5	40.3	39.2	25.7	20.2

[a] Average number of carbon atoms per molecule

BUTENES

The thermal decomposition of the *n*-butenes is a complex process in which polymerization, isomerization and splitting of the carbon chain take place simultaneously. Because of the symmetry of the molecule, 2-butene is the more stable, initial decomposition occurring at 350°C., while with 1-butene the temperature is 25° lower. Since either of the two isomerizes into the other, a study of one is really a study of a mixture of both, according to Egloff and Wilson.[133] Only at low temperatures in the early stages of the decomposition will differences due to the relative stability of the two appear.

Figs. 22 and 23 are graphical representations of the reactions undergone together with the calculated energy of activation. The products from 1-butene may be accounted for by reactions (1), (2) and (7) (Fig. 22) and from 2-butene by (1) and (2) (Fig. 23) although the exact mechanism is unknown. Absence of other possible radicals may be attributed to the fact that such radicals tend to undergo very rapid secondary reactions giving a more stable form.

Wheeler and Wood[134] have found that cyclohexene, cyclohexadiene, methylcyclohexene and methylcyclohexadiene are the chief polymerization products below 650°C., while above this temperature aromatic compounds predominate in the liquids obtained. This is very unusual, as 8-carbon-molecule polymerization products might be expected. However, the formation of the 6- and 7-carbon molecules shows that the free radicals from the primary dissociation, and not the butene molecule as a whole, are polymerized.

The catalytic rearrangement of the *n*-butenes has been studied by Ipatieff, Pines and Schaad.[135] In the presence of orthophosphoric acid, 1-butene undergoes 4 per cent isomerization at 26°C. and 60 per cent at 135°C. A catalyst of diatomaceous earth impregnated with phosphoric acid gives complete conversion to 2-butene at 249°C. and 7.8 atmospheres pressure. Pure *trans*-2-butene underwent rearrangement to the extent of 6.6 per cent to 1-butene and 6.0 per cent to *cis*-2-butene when passed through orthophosphoric acid at 100°C. Aqueous solutions of perchloric acid (70-72 per cent) and benzene sulphonic acid (75 per cent) were also found to effect the transformation of 1-butene, the first giving 21 per cent isomerization at 21°C. and the latter 13 per cent at 76°C.

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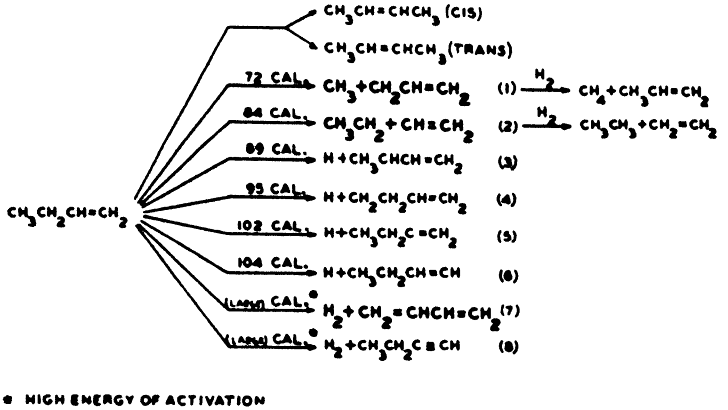
[132] H. Tropsch, C. I. Parrish and G. Egloff, *Ind. Eng. Chem.*, 1936, **28**, 581; *Brit. Chem. Abs.* **A**, 1936, 818; *J. Inst. Pet. Tech.*, 1936, **22**, 255A; *Chem. Abs.*, 1936, **30**, 4147.

[133] G. Egloff and E. Wilson, *Ind. Eng. Chem.*, 1935, **27**, 917; *J. Inst. Pet. Tech.*, 1935, **21**, 369A; *Brit. Chem. Abs.* **A**, 1935, 1206; *Chem. Abs.*, 1935, **29**, 6203.

[134] R. V. Wheeler and W. L. Wood, *J. C. S.*, **1930**, 1819; *Chem. Abs.*, 1930, **24**, 5715; *Brit. Chem. Abs.* **A**, 1930, 1399. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.



Courtesy Industrial and Engineering Chemistry

FIG. 22.—Thermal Reactions of 1-Butene. (G. Egloff and E. Wilson)

Hurd and Goldsby[136] have stated that extensive rearrangement of the gaseous decomposition products of the *n*-butenes occurs at 650°C. The ratio of *cis* to *trans* forms[137] in 2-butene was found to be practically unchanged in the pyrolysis of the latter, indicating that the stereoisomers share equally in whatever changes occur. However, more *cis* than *trans* isomer was found in the 2-butene produced from 1-butene.

The kinetics of the isomerization of *cis*- and *trans*-2-butene at 345-390°C. have been investigated by Kistiakowsky and Smith,[138] who report that the equilibrium mixture consists of 52.8 per cent *trans* compound at these temperatures. Although there was no evidence to indicate polymerization or formation of 1-butene, the mechanism of the reaction is thought to involve a chain because of the abnormalities observed.

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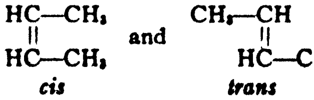
[135] V. N. Ipatieff, H. Pines and R. E. Schaad, *J.A.C.S.*, 1934, **56**, 2696; *Brit. Chem. Abs.* **A**, 1935, 192; *J. Inst. Pet. Tech.*, 1935, **21**, 47A; *Chem. Abs.*, 1935, **29**, 724.

[136] C. D. Hurd and A. R. Goldsby, *J.A.C.S.*, 1934, **56**, 1812; *Brit. Chem. Abs.* **A**, 1934, 1080; *J. Inst. Pet. Tech.*, 1934, **20**, 522A; *Chem. Abs.*, 1934, **28**, 6101.

[137] The two steric modifications of 2-butene are represented as:



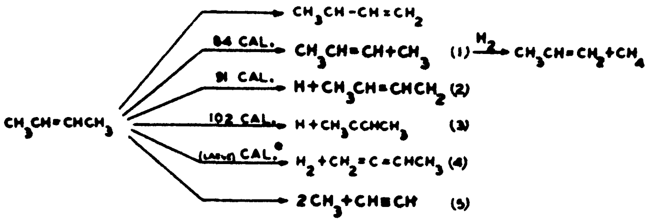
$$\begin{array}{c}HC—CH_3\\ \|\\ HC—CH_3\end{array} \quad \text{and} \quad \begin{array}{c}CH_3—CH\\ \|\\ HC—CH_3\end{array}$$

cis *trans*

[138] G. B. Kistiakowsky and W. R. Smith, *J.A.C.S.*, 1936, **58**, 776; *J. Inst. Pet. Tech.*, 1936, **22**, 299A; *Brit. Chem. Abs.* **A**, 1936, 802; *Chem. Abs.*, 1936, **30**, 5104.

High yields of butadiene have been reported[139] from pyrolysis of 2-butene diluted with an inert gaseous material at about 700°C. Passage of a 7 to 1 mixture of nitrogen and the hydrocarbon through a porcelain tube at this temperature gave a 21 per cent yield of the diolefin with 18-24 per cent decomposition of the butene.

Pyrolysis at 1100°C. in conjunction with low pressure and short contact times is reported to favor the formation of butadiene from both normal butenes.[140] In the case of 1-butene, lower paraffins, hydrogen, acetylene and ethylene are all found in appreciable quantities, as would be expected in accordance with Reactions (1), (2) and (7) (Fig. 22). At 1400°C. with 1-butene, only hydrogen, acetylene and paraffins are obtained in large proportions at contact times greater than 0.0036 second, showing the dominance of Reaction (2). The large yield of acetylene may be attributed to the fact that at this temperature, acetylene formation from ethylene reaches a maximum.[141] In no test, however, was any isobutene obtained. The data for these hydrocarbons are incorporated in Tables 24 and 25.



Courtesy Industrial and Engineering Chemistry

FIG. 23.—Thermal Reactions of 2-Butene. (G. Egloff and E. Wilson)

TABLE 24.—*Pyrolysis of 1-Butene at 50 mm. Pressure.*

Temperature, °C.	1100				1400			
Contact time, 10^{-3} sec.	1.9	3.7	7.9	13.0	0.9	3.6	5.9	9.8
Analysis, %								
C_2H_2	13.4	15.4	15.9	17.3	25.7	22.1	18.4	19.8
C_2H_4	18.5	18.5	20.6	21.1	15.2	2.3	0.7	0.4
$C_3H_6 + C_4H_8$	18.4	6.2	5.5	2.4	1.7	0.0	0.0	0.0
C_4H_6	6.2	10.1	4.1	2.7	—	—	—	—
H_2	15.3	17.8	20.4	27.8	34.3	60 2	66.2	70.8
C_nH_{2n+2}	27.4	31.0	31.8	27.7	20.9	9.6	7.2	2.7
n in Paraffins[a]	1.50	1.70	1.86	1.03	1.45	1.02	2.7	2.2
Yield, liters per 100 l. of 1-butene charged:								
C_2H_2	22.1	26.5	29.4	35.0	64.5	57.6	42.7	50.6
C_2H_4	30.5	31.8	38.1	42.6	38.2	6.0	1.6	1.0
$C_3H_6 + C_4H_8$	30.4	10.7	10.1	4.8	4.3	0.0	0.0	0.0
C_4H_6	10.2	17.4	7.6	5.5	—	—	—	—
H_2	25.2	31.6	37.8	56.1	86.5	157.0	154.0	181.0
C_nH_{2n+2}	45.2	53.2	58.9	55.9	52.5	25.0	16.7	6.8

[a] Average number of carbon atoms per molecule.

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[139] B. P. Fedorov, A. I. Smirnova and P. A. Semenov, *J. Appl. Chem. (U.S.S.R.)*, 1934, 7, 1166; *Brit. Chem. Abs.* A, 1935, 324; *Chem. Abs.*, 1935, **29**, 5808.

[140] H. Tropsch, C. I. Parrish and G. Egloff, *Ind. Eng. Chem.*, 1936, **28**, 581; *Brit. Chem. Abs.* A, 1936, 818; *J. Inst. Pet. Tech.*, 1936, **22**, 255A; *Chem. Abs.*, 1936, **30**, 4147.

[141] G. Egloff and E. Wilson, *Ind. Eng. Chem.*, 1935, 27, 917; *J. Inst. Pet. Tech.*, 1935, **21**, 369A; *Brit. Chem. Abs.* A, 1935, 1206; *Chem. Abs.*, 1935, **29**, 6203.

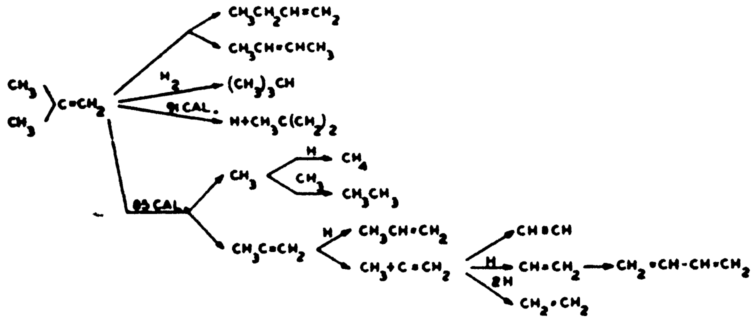
TABLE 25.—*Pyrolysis of 2-Butene at 50 mm. Pressure*

Temperature, °C.	1100					1400			
Contact time, 10^{-3} sec.	1.2	2.5	3.0	5.8	11.0	1.0	1.9	2.8	6.6
Analysis, %									
C_2H_2	6.8	11.3	13.9	13.3	15.4	23.4	23.9	22.3	15.6
C_2H_4	5.6	12.5	16.8	18.6	18.5	5.0	3.7	2.1	0.0
$C_3H_6 + C_4H_8$	53.2	20.0	12.2	8.3	5.5	1.1	0.9	0.6	0.0
C_4H_6	12.6	14.4	9.2	6.2	2.4	—	—	—	—
H_2	7.0	15.0	19.8	21.2	24.0	43.6	51.8	60.3	49.1
C_nH_{2n+2}	14.0	25.7	27.0	29.7	29.1	19.4	18.0	10.3	26.2
n in Paraffins[a]	1.32	1.29	1.02	1.18	1.04	1.3	1.2	1.2	1.3
Yield, liters per 100 l. of 2-butene charged:									
C_2H_2	8.4	18.3	26.0	23.3	25.0	43.5	64.1	56.8	28.1
C_2H_4	7.0	20.2	31.4	32.6	30.2	9.3	9.9	5.4	0.0
$C_3H_6 + C_4H_8$	66.0	32.4	22.8	14.5	9.0	—	—	—	—
C_4H_6	15.6	23.3	17.2	10.8	3.9	—	—	—	—
H_2	8.7	24.3	37.0	37.0	39.1	81.0	139.0	154.0	88.5
C_nH_{2n+2}	17.3	41.6	50.5	52.0	47.5	36.0	48.2	26.3	47.1

[a] Average number of carbon atoms per molecule.

ISOBUTENE

The thermal reactions of isobutene differ from those of the normal butenes or straight-chain olefins. As a result of its unsymmetrical character, the molecule will tend to form more stable substances, either by losing the methyl groups or by adding hydrogen. The latter change and also the formation of propane are favored by relatively low-temperature treatment, and use of higher temperatures is marked by the increase in yields of acetylene and methane.[142] The thermal reactions for isobutene are shown in Fig. 24.



Courtesy Industrial and Engineering Chemistry

FIG. 24.—Thermal Reactions of Isobutene. (G. Egloff and E. Wilson)

Hurd and Eilers[143] have studied the thermal decomposition of this hydrocarbon both from the standpoint of primary products and of catalytic influence of different tube materials. The results of their experiments at temperatures of 700-800°C. are shown graphically in Fig. 25, in which the composition of the gaseous products is compared at various percentage conversions. Extrapolation to zero conversion would seem to indicate that methane, propene and ethylene are the important primary gaseous products, while hydrogen and acetylene are not.[144] Hurd and Eilers, however, believe that ethylene is not actually an initial product but is probably a secondary one derived from propene. An examination of the liquid obtained in pyrolysis at 700°C. showed the following substances: (in per cent) trimethylethylene, 1.2; benzene, 10.3; toluene, 11.8; unsaturated oil b.p. 78-125°C. (diisobutene?), 22.1; naphthalene, 8.75; anthracene, 3.0; unsaturated oils b.p. 125-190°C., 19.5; residue, 23.4. A number of comparative experiments in tubes of different materials show that Ascoloy (a chromium steel alloy), quartz and glass have little influence on the decomposition at 700°C. Monel metal and iron, particularly the former, favor considerable carbonization and entirely suppress oil formation. Similarly, nickel at 700°C. inhibits the production of oil but its catalytic action is less marked than with Monel and iron. Table 26 lists the data obtained in these tests.

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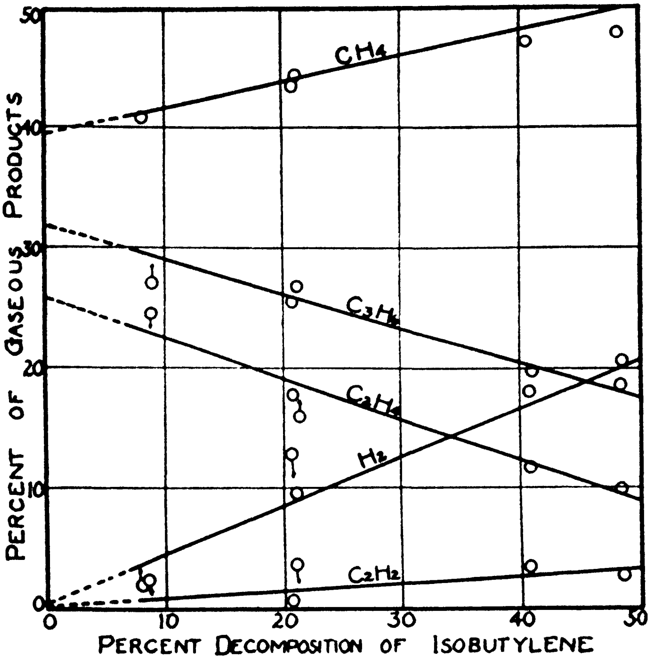
[142] G. Egloff and E. Wilson, *Ind. Eng. Chem.*, 1935, 27, 917; *J. Inst. Pet. Tech.*, 1935, 21, 369A; *Brit. Chem. Abs.* A, 1935, 1206; *Chem. Abs.*, 1935, 29, 6203.

[143] C. D. Hurd and L. K. Eilers, *Ind. Eng. Chem.*, 1934, 26, 776; *Chem. Abs.*, 1934, 28, 5646; *Brit. Chem. Abs.* B, 1934, 792; *J. Inst. Pet. Tech.*, 1934, 20, 493A.



Courtesy Industrial and Engineering Chemistry

FIG. 25.—Gaseous Products from Pyrolysis of Isobutene at 700-800°C. (C. D. Hurd and L. K. Eilers)

The results of the high-temperature-low-pressure pyrolysis of isobutene given by Tropsch, Parrish and Egloff[145] are incorporated in Table *27*. A comparison of Tables 24 to 26 on the three butenes at similar conditions of thermal treatment

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[144] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**, for a discussion of the method of zero extrapolation.

[145] H. Tropsch, C. I. Parrish and G. Egloff, *Ind. Eng. Chem.*, 1936, **28**, 581; *Chem. Abs.*, 1936, **30**, 4147; *Brit. Chem. Abs.* **B**, 1936, 818; *J. Inst. Pet. Tech.*, 1936, **22**, 255A.

TABLE 26.—*Decomposition of Isobutene in Various Tubes.*

	Quartz	Glass	Ascoloy		Iron		Nickel	Monel
Temperature, °C.	700	700	700	700	550	600	700	410
Contact time, sec.	4.1	12	5	9.2	22	5	5.2	16.7
Liquids, % by wt. of isobutene decomposed	62	47	11	22	—	—	—	—
Carbon formed, % by wt.	—	—	—	—	Trace	28	13	33
Extent of decomposition, %	21	30.2	31	33	1.3	25.5	26	24
Analysis of exit gas, % by volume								
Acetylene	0.1	1.2	0.23	0.94	0.0	0.0	0.32	0.0
Isobutene	79.3	63.4	89.29	80.56	98.3	49.2	48.8	45.9
Propene	4.7	6.0	3.47	6.36	0.3	0.7	3.93	1.96
Ethylene	3.3	1.9	3.58	4.24	0.9	1.3	5.41	2.27
Hydrogen	2.4	6.7	1.05	2.00	0.0	44.8	31.95	48.26
Paraffins	7.9	19.7	2.46	5.90	0.0	2.0	8.49	1.55
n in Paraffins[a]	1.5	1.59	1.6	1.4	—	1.9	1.55	—

[a] Average number of carbon atoms per molecule.

TABLE 27.—*Pyrolysis of Isobutene at 50 mm. Pressure.*

Temperature, °C.	1100				1400		
Contact time, 10^{-3} sec.	1.3	4.0	7.1	11.0	0.8	1.8	3.1
Analysis, %							
C_2H_2	7.8	16.5	18.6	17.6	19.8	20.6	20.2
C_2H_4	1.1	8.8	7.7	8.8	5.3	2.8	0.0
$C_3H_6 + C_4H_8$	16.1	9.2	6.1	11.6	1.2	0.4	0.0
C_4H_6	4.1	4.0	2.2	2.1	0.3	0.0	0.0
iso-C_4H_8	46.1	3.4	1.1	0.0	0.0	0.0	0.0
H_2	5.2	14.4	16.9	21.9	39.3	55.0	62.7
C_nH_{2n+2}	18.1	40.0	42.8	35.0	26.6	18.5	11.2
n in C_nH_{2n+2}	1.27	1.33	1.08	1.66	1.4	1.15	1.25
Yield, liters per 100 l. of isobutene charged:							
C_2H_2	9.2	37.6	31.6	30.2	38.6	57.8	48.1
C_2H_4	1.3	20.1	13.1	15.1	10.3	7.9	0.0
$C_3H_6 + C_4H_8$	19.0	21.0	10.3	19.1	2.3	0.0	0.0
C_4H_6	4.9	9.1	3.7	3.6	0.6	0.0	0.0
H_2	6.1	32.8	28.7	36.3	74.6	154.0	149.0
C_nH_{2n+2}	21.4	91.2	72.9	60.1	51.8	52.0	26.0

shows the importance of the relation of structure to decomposition products. In the case of the branched hydrocarbon, the production of paraffins (mostly methane), acetylene and hydrogen predominate whereas ethylene, which was major resultant in the normal compounds is relatively unimportant. The yield of butadiene is quite good, but is slightly below that obtained with the other two butenes.

HIGHER MONOLEFINS

It has been shown by Hurd, Goodyear and Goldsby[146] that partial isomerization of 1-pentene into 2-pentene, and vice versa, takes place during the pyrolysis of these hydrocarbons at temperatures above 580°C. at atmospheric pressure. The gaseous products from both pentenes consisted of methane, 1-butene, propene, ethane and ethylene in the molar proportions 6, 2, 2, 2, 1, respectively. In addition, small amounts of 2-butene, butadiene and hydrogen resulted. 2-Pentene was found to be somewhat more stable than 1-pentene under these conditions.

[146] C. D. Hurd, G. H. Goodyear and A. R. Goldsby, *J.A.C.S.*, 1936, **58**, 235; *J. Inst. Pet. Tech.*, 1936, **22**, 255A; *Brit. Chem. Abs.* A, 1936, 451; *Chem. Abs.*, 1936, **30**, 2911.

The pyrolysis of 2-pentene in glass, Ascoloy and iron tubes at 560-700°C. has been investigated by Hurd and Eilers.[147] In iron tubes, pronounced carbonization with total suppression of oil formation occurred even at 560°C. Ascoloy did not appear to catalyze the decomposition to any appreciable extent. In glass or Ascoloy tubes at 600-700°C. the main gaseous products were methane, ethane, propene and butenes, with only small amounts of hydrogen. The butene fraction consisted principally of 1-butene, with smaller amounts of 2-butene, isobutene and butadiene. Benzene, toluene and various unsaturated hydrocarbons were contained in the liquid fraction.

Isomerization of 1-hexene has been shown to take place by heating at 400°C. and 140 atmospheres pressure for 1 hour, giving rise to 2-hexene and 3-hexene, but no isohexenes. In the presence of molybdenum sulphide, 1-hexene commences to polymerize at 350°C. and normal pressure.[148] The thermal decomposition of 1-hexene in an excess of water vapor at 550-700°C. has yielded 40 per cent ethylene, 30 per cent propene and 4.3 to 5.8 per cent butadiene. Like treatment of 4-methyl-1-pentene gave 58-60 per cent propene.[148a]

When *ter*-butylethylene is heated to 160-170°C. in the presence of floridin, it is converted into tetramethylethylene, according to Lebedev and Kudrjavtzev.[149] At 150-270°C. *ter*-butylmethylethylene changes into trimethylethylethylene under the influence of this catalyst, while *ter*-butylacetylene, tetramethylethylene and trimethylethylethylene are unaffected by similar treatment, even up to 300°C.

Lebedev and Slobodin[150] found that the passage of diisobutylene over a floridin catalyst at 205-210°C., at a velocity of 0.4 to 0.45 g. per minute, resulted in a yield of 70 per cent of diisocrotyl (2,5-dimethyl-2,4-hexadiene). Hurd and Eilers[151] have pyrolyzed both technical diisobutylene (a mixture of 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene) and pure 2,4,4-trimethyl-2-pentene in Pyrex tubes at 700°C. The pure hydrocarbon decomposed more rapidly than the technical mixture and furnished a gas containing large portions of isobutene. The mixture, instead, yielded a gas consisting chiefly of methane and hydrogen, with only 5 to 8 per cent of isobutene. The liquid products showed the formation of small amounts of aromatic hydrocarbons (much less than in the case of isobutene under similar conditions) and also large proportions of unsaturated liquids with boiling ranges both below and above that of the diisobutylene used. Hurd and Eilers concluded that diisobutylene need not be regarded as an essential intermediate in the thermal polymerization of isobutene.

Certain large molecular weight monolefins with highly branched chains undergo cleavage under special conditions with the production of a mixture of lower olefins. Nazarov[152] has studied the splitting of several of these hydrocarbons, including di-*ter*-butylethylene, under the influence of 1-bromonaphthalene-4-sulphonic acid and similar acids. Unsymmetrical dimethylethylene is the chief product, with smaller amounts of tetramethylethylene, isopropylmethylethylene and *ter*-butylethylene.

Pinene. Thermal decomposition of turpentine oil, which consists mainly of two isomeric dicyclic monolefins, is of interest since it has been used as a source of isoprene. Mahood[153] noted that a maximum yield of isoprene of about 4.5 per cent may be obtained by pyrolysis in a Pyrex tube at 600°C. and in an iron tube at 450°C. Finely divided copper has been recommended as a catalyst for decomposition to aromatics (which may consume as high as 31 per cent of the pinene) at 500 to 630°C.[154] Toluene, *m*-xylene, cymene, cumene and methylethylbenzene have been obtained in this fraction. Nickel causes an energetic reaction at 600°C. with the deposition of much carbonaceous material, a gas rich in hydrogen and but little liquid. Cobalt is intermediate between copper and nickel in its action, but iron resembles nickel and causes intense carbonization.

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[147] C. D. Hurd and L. K. Eilers, *Ind. Eng. Chem.*, 1934, **26**, 776; *Brit. Chem. Abs.* **B**, 1934, 792; *Chem. Abs.*, 1934, **28**, 5646; *J. Inst. Pet. Tech.*, 1934, **20**, 493A.

[148] A. D. Petrov, A. P. Meshcheriakov and D. N. Andreev, *Ber.*, 1935, **68**, 1; *Chem. Abs.*, 1935, **29**, 2145; *Brit. Chem. Abs.* **A**, 1935, 324.

[148a] B. M. Mikhailov and Yu. A. Arbuzov, *Compt. rend. acad. sci. U.R.S.S.*, 1936, **3**, 423; *Chem. Abs.*, 1937, **31**, 1354; *Brit. Chem. Abs.* **B**, 1936, 1485.

[149] S. V. Lebedev and N. A. Kudrjavtzev, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 1859; *Brit. Chem. Abs.* **A**, 1936, 702; *Chem. Abs.*, 1936, **30**, 3402.

[150] S. V. Lebedev and Y. M. Slobodin, *J. Gen. Chem. (U.S.S.R.)*, 1934, **4**, 23; *Chem. Abs.*, 1934, **28**, 5399; *Brit. Chem. Abs.* **A**, 1934, 864.

[151] C. D. Hurd and L. K. Eilers, *loc. cit.*

[152] I. N. Nazarov, *Ber.*, 1936, **69**, 18, 21; *Chem. Abs.*, 1936, **30** 2014; *Compt. rend. acad. sci., U.R.S.S.*, 1936, **1**, 79; *Brit. Chem. Abs.* **A**, 1936 588

DIOLEFINS

Extensive information on the thermal reactions of diolefins is apparently not available. The lowest member of the series (allene, $CH_2{=}C{=}CH_2$) is an isomer of both methylacetylene and cyclopropene. Isomerization of these three hydrocarbons, involving the shifting of hydrogen atoms in the molecule (which requires only a small energy of activation), should occur at low temperatures.[155] Likewise, because of the unsaturated nature of the series, polymerization of the diolefins should be expected, since the double bonds are conducive to this type of reaction, provided the compounds are not of high molecular weight.[156]

Slobodin[157] reports that methylallene begins to isomerize at 250°C. under the influence of activated floridin, and at 330°C. undergoes 24.5 per cent rearrangement. The products obtained at the higher temperature were 20.6 per cent bivinyl and 3.9 per cent ethylacetylene ($C_2H_5C{\equiv}CH$). Dimethylacetylene was not detected, nor were any traces of dimers of bivinyl or methylallene. Unsymmetrical dimethylallene with activated floridin at 334°C. gives isoprene and isopropylacetylene, $(CH_3)_2CHC{\equiv}CH$, in 20.8 and 60 per cent conversions, respectively. Partial polymerization may also take place; resulting chiefly in a dimer of isoprene.[158]

Lebedev and Slobodin[159] obtained a 41.5 per cent yield of dipropenyl by 6 recirculations of diallyl (1,5-hexadiene) over a floridin catalyst at 225°C. The isomerization was accompanied by a partial polymerization of the hydrocarbons.

ACETYLENE

According to Egloff and Wilson, the reactions of pure acetylene should differ considerably from those observed with this hydrocarbon when it is a secondary decomposition product of ethylene. The reason for this is probably because of the small concentration of acetylene molecules in the latter instance, due to the dilution with other molecules. Dissociation should take place through the same mechanisms, but the chances for methenyl (CH≡) radical formation are much greater.[160] Aromatic hydrocarbons, carbon, hydrogen and methane are the main products at 650°C. or over.[161]

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[153] S. A. Mahood, *Ind. Eng. Chem.*, 1920, 12, 1152; *J.C.S.*, 1921, 120 (1), 116; *Chem. Abs.*, 1921, 15, 519.

[154] P. Sabatier, A. Mailhe and G. Gaudion, *Compt. rend.*, 1919, 168, 926; *Chem. Abs.*, 1919, 13, 1838; *J.C.S.*, 1919, 116 (1), 336.

[155] G. Egloff and E. Wilson, *Ind. Eng. Chem.*, 1935, 27, 917; *J. Inst. Pet. Tech.*, 1935, 21, 369A; *Brit. Chem. Abs.* A, 1935, 1206; *Chem. Abs.*, 1935, 29, 6203.

[156] R. E. Meinert and C. D. Hurd, *J.A.C.S.*, 1930, 52, 4540; *Brit. Chem. Abs.* A, 1931, 61; *Chem. Abs.*, 1931, 25, 68. See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. See also Chapter 26.

[157] Y. M. Slobodin, *J. Gen. Chem. (U.S.S.R.)*, 1935, 5, 48; *Chem. Abs.*, 1935, 29, 4732; *Brit. Chem. Abs.* A, 1935, 957.

[158] Y. M. Slobodin, *J. Gen. Chem. (U.S.S.R.)*, 1934, 4, 778; *Chem. Abs.*, 1935, 29, 2145; *Brit. Chem. Abs.* A, 1935, 62.

[159] S. V. Lebedev and Y. M. Slobodin, *J. Gen. Chem. (U.S.S.R.)*, 1934, 4, 23; *Chem. Abs.*, 1934, 28, 5399; *Brit. Chem. Abs.* A, 1934, 864.

Because of its highly unsaturated nature, acetylene polymerizes very readily in the range of 400° to 800°C. Mignonac and Ditz[162] obtained, along with other products, two gases corresponding to the empirical formula of butenyne (C_4H_4) by passing acetylene rapidly through a narrow-bore silica tube at 750°C. The gases were cooled to —70°C., and liquefied, one into a colorless stable carbide (having the above formula), and the other into a substance known as chlorene (a polymer of C_4H_4), a greenish-yellow gas, which on standing was converted into the first. These substances may be linear polymers of the type obtained by Mignonac and de Saint-Aunay[163] by the action of the electric discharge on acetylene at low temperatures.

Travers[164] found that at 450°C. the addition of hydrogen to acetylene greatly influences the rate of reaction. Large concentrations of hydrogen suppress the formation of ethylene but do not change the yield of methane. The reaction velocity is decidedly affected by the surface conditions, as in the case of ethylene and ethane.

Aromatics have been obtained in good yields by Klatt[165] by passage of acetylene diluted with 10 per cent of steam through a porcelain tube at 650 to 700°C. and atmospheric pressure. Several runs were made, using coke, graphite, porcelain and earthenware fragments as packing, but the maximum conversion to liquids resulted with contact material consisting of graphitic carbon deposited on pieces of clay plate. Fujio[166] likewise reports good yields of aromatics by passing acetylene through an iron tube lined with silicon or an alloy of chromium and silicon, heated to about 650°C.

CYCLIC HYDROCARBONS

Of the monocyclic saturated hydrocarbons those containing the cyclopentane and cyclohexane rings are by far the most heat-stable and differ greatly from the corresponding paraffins in this respect. This property complicates the study of primary reactions, since the initial products may be decomposed even under conditions where little of the cycloparaffin is converted.[167]

However, the lower members of the series, such as cyclopropane and cyclobutane hydrocarbons, exhibit a tendency to undergo rupture of the ring, especially with the aid of such catalysts as alumina, at relatively low temperatures with the formation of the corresponding straight-chain olefin. Cycloparaffins of more than 6 carbon atoms are less stable than cyclopentane and cyclohexane.[168] Cyclohexane derivatives are characterized by the fact that with such catalysts as nickel

[160] G. Egloff and E. Wilson, *Ind. Eng. Chem.*, 1935, **27**, 917; *J. Inst. Pet. Tech.*, 1935, **21**, 369A; *Brit. Chem. Abs.* **A**, 1935, 1206; *Chem. Abs.*, 1935, **29**, 6203.

[161] It has been shown by A. V. Frost (*Khimteoret, Leningrad*, **1935** (2), 98; *Chem. Abs.*, 1935, **29**, 5626) that whereas synthesis of acetylene from its elements sets in above 2500°K. (2227°C.), the formation of this hydrocarbon from others proceeds at much lower temperatures, at which acetylene is thermodynamically unstable.

[162] G. Mignonac and E. Ditz, *Compt. rend.*, 1934, **199**, 367; *Chem. Abs.*, 1934, **28**, 6697; *Brit. Chem. Abs.* **A**, 1934, 990. See also Chapter 28.

[163] G. Mignonac and R. V. de Saint-Aunay, *Compt. rend.*, 1929, **189**, 106; *Chem. Abs.*, 1929, **23**, 4668; *Brit. Chem. Abs.* **A**, 1929, 537.

[164] M. W. Travers, *Trans. Faraday Soc.*, 1936, **32**, 236; *Chem. Abs.*, 1936, **30**, 2548; *Brit. Chem. Abs.* **A**, 1936, 309.

[165] R. Klatt, *Erdöl u. Teer*, 1934, **10**, 241, 253, 265; *Chem. Abs.*, 1934, **28**, 7243; *J. Inst. Pet. Tech.*, 1934, **20**, 487A.

[166] S. Fujio, Japanese P. 109,263, 1935, to the Minister of Navy; *Chem. Abs.*, 1935, **29**, 3692.

[167] F. E. Frey, *Ind. Eng. Chem.*, 1934, **26**, 198; *J. Inst. Pet. Tech.*, 1934, **20**, 158A; *Brit. Chem. Abs.* **B**, 1934, 438; *Chem. Abs.*, 1934, **28**, 2169.

[168] A. Baeyer, *Ber.*, 1885, **18**, 2269; *J.C.S.*, 1885, **48**, 1108. W. H. Carothers, *J.A.C.S.*, 1929, **51**, 2548; *Brit. Chem. Abs.* **A**, 1929, 1165; *Chem. Abs.*, 1929, **23**, 4438.

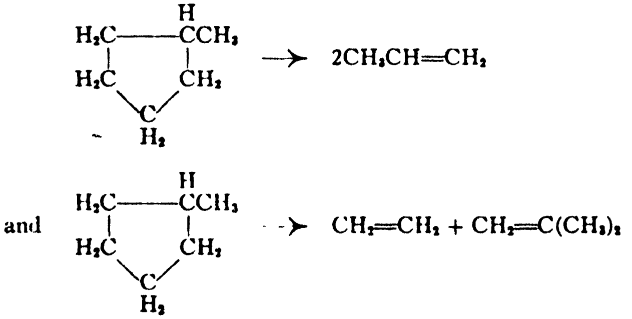
or palladium they can be dehydrogenated to the corresponding aromatic hydrocarbons and that this process is reversible.[169]

Cyclopropane. Chambers and Kistiakowsky[170] have investigated the kinetics of the thermal isomerization of cyclopropane into propene in a static system over the range 470-519°C. The reaction was found to be homogeneous and apparently unimolecular, the relation between the high-pressure velocity constant and temperature being represented by the equation:[171]

$$\log_{10} k = 15.17 - \frac{65{,}000}{2.3RT}$$

Cyclopentane. The results obtained by Frey[172] indicate that this hydrocarbon undergoes decomposition in a silica tube at 575°C. at a rate only about one-sixth as great as that of *n*-pentane under the same conditions. At 574°C. and a pressure of 67 mm., with a contact time of 10 minutes, the dissociation amounted to 22 per cent, and from 100 moles of cyclopentane there were produced (in moles): hydrogen, 23; methane, 5; ethylene, 20; ethane, 2; propene, 27; propane, 2; cyclopentadiene and cyclopentene, 16; and higher hydrocarbons, 6. It appears, therefore, that the two main reactions involved are (1) dehydrogenation to cyclopentene and cyclopentadiene, and (2) rupture of the carbon ring to form ethylene and propene. Kazanskii and Plate[173] substantiate this mechanism by a study of the pyrolysis at 590-800°C. in silica tubes using contact times of 0.5 to 20 seconds.

Methylcyclopentane. In the decomposition of this hydrocarbon at 650°C., Kazanskii and Plate[174] obtained gaseous products consisting chiefly of propene with some isobutene. The content of saturated hydrocarbons was higher than in the gas produced by pyrolysis of cyclopentane, probably as a result of the splitting of methane from some of the products. The two main reactions appear to be:



Other Cyclopentane Derivatives. Although in the presence of aluminum chloride, containing small amounts of water, methylcyclopentane is readily converted into cyclohexane,[175] even at low temperatures, when passed over platinum charcoal (18 per cent Pt) at 310-350°C., as noted by Nenitzescu and Cioranescu,[176] the former hydrocarbon is unchanged. Likewise, Tarasova[177] states that neither the ethyl, propyl, butyl, 1,2-dimethyl, 1-methyl-2-ethyl nor 1-methyl-2-propyl derivatives of cyclopentane are dehydrogenated in the presence of platinum charcoal in a stream of hydrogen or carbon dioxide even at 300°C.

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[169] N. Zelinskii and N. Pavlov, *Ber.*, 1923, **56**, 1249; *Chem. Abs.*, 1923, **17**, 3124; *J.C.S.* 1923, **124** (1), 767.

[170] T. S. Chambers and G. B. Kistiakowsky, *J.A.C.S.*, 1934, **56**, 399; *Chem. Abs.*, 1934, **28**, 2252; *Brit. Chem. Abs.* A, 1934, 369; *J. Inst. Pet. Tech.*, 1934, **20**, 238A.

[171] *Cf.* M. Trautz and K. Winkler, *J. prakt. Chem.*, 1922, (2) **104**, 53; *Chem. Abs.*, 1923, **17**, 722; *J.C.S.*, 1922, **122** (1), 926.

[172] F. E. Frey, *loc. cit.*

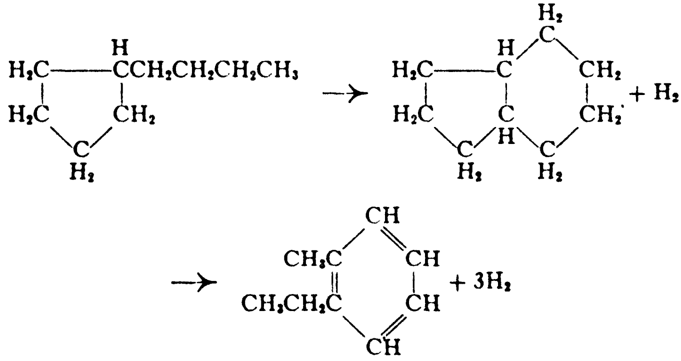
[173] B. A. Kazanskii and A. F. Plate, *Ber.*, 1934, **67**, 1023; *Brit. Chem. Abs.* A, 1934, 877; *Chem. Abs.*, 1934, **28**, 5048.

[174] B. A. Kazanskii and A. F. Plate, *loc. cit.*

[175] C. D. Nenitzescu and I. P. Cantuniari, *Ber.*, 1933, **66**, 1097; *Chem. Abs.*, 1933, **27**, 4780; *Brit. Chem. Abs.* A, 1933, 941. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, 1934. See also Chapter 54.

[176] C. D. Nenitzescu and E. Cioranescu, *Ber.*, 1936, **69**, 1040; *Brit. Chem. Abs.* A, 1936, 831; *Chem. Abs.*, 1936, **30**, 4824.

On the other hand, the work of Zelinskii, Kazanskii and Plate[178] shows that methyl, ethyl and propyl-cyclohexane are readily converted into members of the paraffin series in the presence of hydrogen and platinized charcoal at 305-315°C. The reaction involved is thought to consist only of opening the ring, resulting in the formation of both normal and isoparaffins. Decomposition of the two lower members of the series was not believed to be of a complicated nature, because of the boiling range of the reaction mixture. However, from propylcyclopentane, appreciable quantities of lower molecular weight hydrocarbons were obtained. Subsequent investigations[179] with *n*-butyl-, *sec*-butyl- and isoamyl-cyclopentanes show that under the same conditions, not only paraffins but also aromatics are formed. In fact, aromatization could still be distinctly detected while hydrogenation to paraffins occurred to only a slight extent. Kazanskii and Plate point out that although the aromatic hydrocarbons might have been formed by expansion of the ring at the expense of the side chain, yet, if this is the mechanism involved, then it is difficult to understand why methylcyclopentane and the other lower homologs failed to undergo transformation to aromatics. They therefore suggest another possibility, that is, that a 6-membered ring is formed by closure of the butyl side chain, with the resulting hydrindane then changing into *o*-methylethylbenzene with the opening of the 5-membered ring, as for example:



The first mechanism mentioned above, that involving ring enlargement, should give only monosubstituted derivatives, whereas the latter (involving the rupture of the cyclopentane ring) would form disubstituted benzene homologs. A study of the products obtained from butylcyclopentane showed that the principal resultant was a methylethylbenzene, with a small amount of a monosubstituted aromatic, which upon oxidation gave benzoic acid. A branched paraffin, thought to be 4-methyloctane, was also isolated from the reaction mixture.

Denisenko[180] has investigated the stability of phenylcyclopentane at 300-310°C. in the presence of platinized active charcoal (12 to 15 per cent Pt) and hydrogen. He reports that under these conditions the 5 membered ring is ruptured more readily than is cyclopentane. From the composition of the reaction mixture, which contained 1-phenylpentane (amylbenzene), 2-phenylpentane and 3-phenylpentane, the formation of these substances is explicable on the basis that the ring splits between the 1,2- 2,3- or 3,4- carbon atoms accompanied by the addition of one molecule of hydrogen. Such a transformation may be illustrated as follows:

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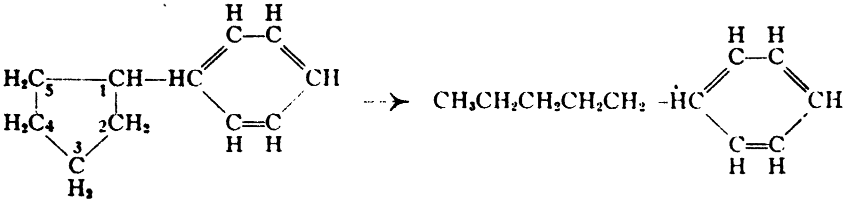
[177] E. M. Tarasova, *Uchenuie Zapiski (Wiss. Ber. Moskau Staats-Univ.)*, 1934, **3**, 173; *Chem. Zentr.*, 1935, **2**, 3497; *Chem. Abs.*, 1936, **30**, 8173.

[178] N. D. Zelinskii, B. A. Kazanskii and A. F. Plate. *Ber.*, 1935, **68**, 1869; *Chem. Abs.*, 1935, **29**, 7950; *Brit. Chem Abs.* A, 1935, 1357.

[179] B. A. Kazanskii and A. F. Plate, *Ber.*, 1936, **69**, 1862; *Chem. Abs.*, 1936, **30**, 6713; *Brit. Chem. Abs.* A, 1936, 1238.

[180] Yu. I. Denisenko, *Ber.*, 1936, 69, 1353; *Chem. Abs.*, 1936, **30**, 5570.



Cyclohexane. Catalytic dehydrogenation of cyclohexane to benzene proceeds smoothly when aided by such metals as nickel or palladium.[181] With a nickel-alumina catalyst at 200-270°C., the energy of activation is about 13,600 cal. per mole for the dehydrogenation of both cyclohexane and methylcyclohexane, although the reaction is much more rapid in the latter case.[182] It has been noted, however, that with the latter catalyst at 330-350°C., cyclohexane in the presence of hydrogen undergoes a peculiar conversion with the formation of not only benzene but also methane, toluene, xylene, methyl- and dimethylcyclohexane. Ipatieff and Komarewsky[183] have identified biphenyl among the reaction products. Zelinskii and Shuikin[184] believe that in addition to undergoing dehydrogenation to benzene, part of the cyclohexane decomposes to form methylene radicals, which are either reduced to methane or combined with benzene and unchanged cyclohexane.

Balandin and Brussov[184a] point out that there are two classes of catalysts in this reaction. Such metals as platinum, palladium and nickel at about 300°C. cause dehydrogenation of 6-membered rings to aromatic nuclei. Oxides of chromium, molybdenum and zinc, employed at 450°C., may give intermediate products, such as cyclohexene or cyclohexadiene.

There is ample evidence to prove that, in the purely thermal decomposition of cyclohexane, direct dehydrogenation to benzene is not the primary process. Butadiene and ethylene appear to be the most important products, although these may subsequently be converted into aromatic hydrocarbons by secondary reactions. Thus, Zelinskii, Mikhailov and Arbuzov[185] pyrolyzed cyclohexane, admixed with an excess of steam (1.5 to 4 volumes), to obtain at 750°C. a molar conversion of 92 per cent to ethylene and 39.9 per cent to butadiene. Kazanskii and Plate[186] reported that at 650°C. in silica tubes the gaseous products were mostly hydrogen, lower paraffins, ethylene and a little isobutene. Whitby and Katz[187] cite a 60.8 per cent conversion to butadiene (based on cyclohexane decomposed) by noncatalytic processes.

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[181] N. Zelinskii and N. Pavlov, *loc. cit.*

[182] A. A. Balandin and A. M. Rubinshtein, *Z. physik. Chem.*, 1934, **A167**, 431; *Chem. Abs.*, 1934, **28**, 2255; *Brit. Chem. Abs.* A, 1934, 371. The kinetics of the catalytic dehydrogenation of methylcyclohexane on a nickel alumina catalyst have been investigated by A. A. Balandin and N. I. Shuikin. *Acta Physicochim., U.R.S.S.*, 1934. **1**, 200; *Chem. Abs.*, 1935, **29**. 6130.

[183] V. N. Ipatieff and V. I. Komarewsky, *J.A.C.S.*, 1936, **58**, 922; *J. Inst. Pet. Tech.*, 1936, **22**, 395A; *Brit. Chem. Abs.* A, 1936, 975; *Chem. Abs.*, 1936, **30**, 5189.

[184] N. D. Zelinskii and N. I. Shuikin, *Compt. rend. acad. sci., U.R.S:S.*, 1934, **3**, 255; *Chem. Abs.*, 1934, **28**, 7252; *Brit. Chem. Abs.* A, 1934, 1209.

[184a] A. A. Balandin and J. J. Brussov, *Z. physik. Chem.*, 1936, **B34**, 96; *Chem. Abs.*, 1937, **31**, 600.

[185] N. D. Zelinskii, B. M. Mikhailov and Y. A. Arbuzov, *J. Gen. Chem. (U.S.S.R.)*, 1934, **4**, 856; *Compt. rend. acad. sci., U.R.S.S.*, 1934, **4**, 208; *Chem. Abs.*, 1935, **29**, 2152; *Brit. Chem. Abs.* A, 1935, 73.

[186] B. A. Kazanskii and A. F. Plate, *Ber.*, 1934, **67**, 1023; *Brit. Chem. Abs.*, A, 1934, 877; *Chem. Abs.*, 1934, **28**, 5048.

[187] G. S. Whitby and M. Katz, *Ind. Eng. Chem.*, 1933, **25**, 1338; *Brit. Chem. Abs.* B, 1934, 158; *Chems. Abs.*, 1934, **28**, 2217. See also P. P. Borisov, E. M. Shakhnazarova and E. I. Margolis. *J. Gen. Chem. (U.S.S.R.)*, 1934, **4** ,1385; *Chem. Abs.*, 1935, **29**, 3648; *Brit. Chem. Abs.* A, 1935, 727.

By treatment of cyclohexane at 622°C. and 68 mm. pressure, Frey[188] obtained 24 per cent decomposition. A mixture of liquid and gaseous products had the following percentage molar composition: hydrogen, 8.1; methane, 3.3; ethylene, 8.4; ethane, 3.7; propene, 5.6; butadiene, 5.6; butenes, 5.0; pentenes, 1.6; unchanged cyclohexane, 57.0; hexenes and hexadienes, 2.1; higher hydrocarbons, 0.5; and benzene, 0.4. It is evident that under these conditions, benzene production is almost negligible and that hydrogen, ethylene, butadiene and butenes are the main reaction products.

On the other hand, chromium-copper catalysts at 500-550°C. are said to cause only dehydrogenation, forming 80 per cent aromatic compounds.[189] Other catalysts, for example, alumina, alumina-zinc chloride and alumina-phosphoric acid are less effective, giving rise to some gaseous and liquid saturated and unsaturated hydrocarbons and partly isomerized paraffins.

Investigations on the decomposition of cyclohexane at 600 to 700°C. indicate that the compound is progressively dehydrogenated, first to tetrahydrobenzene (cyclohexene), then to dihydrobenzene (cyclohexadiene) and finally to benzene itself.[190] Decomposition of the tetrahydrobenzene may also proceed in another manner to yield butadiene and ethylene. The formation of naphthalene in this reaction is believed to be the result of polymerization and condensation of free radicals formed in the energetic decomposition of the cyclohexane.

Other Cyclic Hydrocarbons. Relatively high conversion of both saturated and unsaturated cyclohydrocarbons into butadiene and isoprene has been obtained by pyrolysis of these hydrocarbons admixed with steam as diluent.[191] For example, the yields of butadiene (expressed as molar percentages of the hydrocarbons decomposed) from methylcyclohexane, ethylcyclohexane and decalin at 750°C. were 34.8, 41.2 and 11.6, respectively. Cyclohexene at 650°C. gave molar yields of 78.3 per cent ethylene and 65.2 per cent butadiene, whereas 1-methylcyclohexene at 690°C. furnished 75.1 mole per cent ethylene and 35.3 mole per cent isoprene.

Ethylcyclohexane undergoes decomposition similar to that of cyclohexane in the presence of a nickel oxide-aluminum contact agent at 350°C., according to Ipatieff and Komarewsky.[192] Benzene, toluene, methane and hydrogen were found in the reaction mixture.

The dimethylcyclohexanes have been pyrolyzed at 675-750°C. in the presence of 2 to 4 times their weight of water by Arbuzov and Mikhailov.[193] Conversions to butadiene, in mole per cent of the hydrocarbon decomposed, were: from 1,2-dimethylcyclohexane, 20.7; from 1,3-dimethylcyclohexane, 18.4 and from 1,4-dimethylcyclohexane, 23.9. Large amounts of ethylene, propene and butene and saturated hydrocarbons were also obtained.

Levina and Tzurikov[194] found that vinylcyclohexane when passed over a palladium asbestos catalyst at 200°C., was converted into ethylbenzene and ethylcyclohexane. Analogous to this, allylcyclohexane gave propylbenzene and propylcyclohexane under the same conditions. Subsequent investigations[195] show that the isomers allylcyclohexene, cyclohexylallene and cyclohexylallylene when contacted

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[188] F. E. Frey, *loc. cit.*

[189] V. I. Karzhev, V. I. Sever'yanova and A. N. Sivova, *J. Applied Chem. (U.S.S.R.)*, 1936, **9**, 269; *Chem. Abs.*, 1936, **30**, 5570.

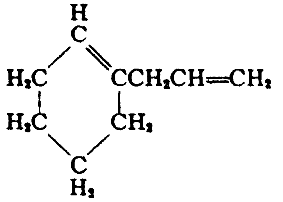
[190] E. Terres, C. Walther, H. Schmidt, J. Pomeraniec and O. Focsaner, *Oel u. Kohle*, 1934, **2**, 2, 53; *Chem. Abs.*, 1935, **29**, 6743; *Brit. Chem. Abs.* **B**, 1935, 391.

[191] N. D. Zelinskii, B. M. Mikhailov and Y. A. Arbuzov, *J. Gen. Chem. (U.S.S.R.)*, 1934, **4**, 856; *Chem. Abs.*, 1935, **29**, 2152; *Brit. Chem. Abs.* **A**, 1935, 73.

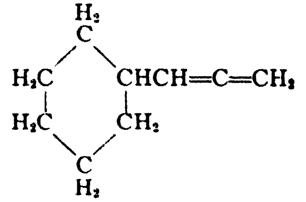
[192] V. N. Ipatieff and V. I. Komarewsky, *J.A.C.S.*, 1936, **58**, 922; *J. Inst. Pet. Tech.*, 1936, **22**, 395A; *Brit. Chem. Abs.* **A**, 1936, 975; *Chem. Abs.*, 1936, **30**, 5189.

[193] Y. A. Arbuzov and B. M. Mikhailov, *Compt. rend. acad. sci., U.R.S.S.*, 1935, **4**, 337; *Brit. Chem. Abs.* **A**, 1936, 712; *Chem. Abs.*, 1936, **30**, 4472.

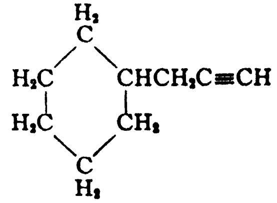
[194] R. Y. Levina and F. F. Tzurikov, *J. Gen. Chem. (U.S.S.R.)*, 1934, **4**, 1250; *Brit. Chem. Abs.* **A**, 1935, 611; *Chem. Abs.*, 1935, **29**, 3314.



allylcyclohexene



cyclohexylallene



cyclohexylallylene

with platinum-carbon agents (containing about 30 per cent Pt) at 200-205°C. in a weak current of carbon dioxide are completely decomposed into identical products of irreversible catalysis, namely, 35 per cent propylcyclohexane and 65 per cent propylbenzene. The mechanism of the conversion is explained by isomerization with a transposition of the double bond into the ring, thus forming an intermediate cyclohexene or cyclohexadiene structure, which immediately undergoes further reaction. The acetylenic side chain is believed to isomerize to the allene type, and then react as above.

The dehydrogenation of 7- and 8-carbon rings to aromatic hydrocarbons has been investigated by Ruzicka and Seidel.[196] Using selenium or palladium charcoal, at 390-440°C. cycloheptane was readily converted into toluene, and cyclooctane to *p*-xylene. The mechanism may have involved ring opening followed by closure to a smaller ring or by closure followed by cleavage. Heating methylcycloheptane with selenium for 27 hours at 440°C. resulted in the production of a mixture of ethylbenzene and *o*- and *p*-xylene. The formation of these substances is explicable on the basis of rupture of the 7-membered ring and subsequent closure between the various positions relative to the attached methyl group. Treatment of 1,1,4-trimethylcycloheptane gave *p*-methylethylbenzene and 1,2,3-trimethylbenzene, whereas 1,1,4-trimethylcycloheptene under similar conditions formed a hydrocarbon which, on oxidation with potassium permanganate, gave isophthalic acid (indicating a 1,3 structure).

Selenium and palladium charcoal are said to be very effective in causing ring increments, especially in the case of a 6-carbon ring from a cyclopentane derivative, as is evidenced from the ready conversion of 1- or 2-methylhydrindene into naphthalene at 450°C. with these catalysts.[197] Likewise naphthalene can be obtained from 1- and 2-ethylhydrindene, 1-*iso*-octylhydrindene and methylisopropylhexahydrofluorene or 1,2-diethylcyclohexene-1 with selenium at 420°C. The yields of naphthalene varied from 5 to 50 per cent and were generally twice as great with selenium as with palladium. The methyl derivatives give the largest proportion of naphthalene, and, in general, the conversion to aromatics decreases with increased complexity of the hydrocarbon. However, at temperatures above 350°C., secondary reactions, such as those involving the cleavage of alkyl chains, become quite prominent. In view of this decomposition, Ruzicka and Peyer point out that at temperatures in excess of 400°C., the results obtained in the aromatization of cyclopentane derivatives require careful interpretation. Nenitzescu and Cioranescu[198] also report the formation of amounts of naphthalene from both 1-methylhydrindene and 1-methylhexahydrohydrindene using platinum charcoal at 310-350°C. By passing indene or hydrindene over dehydrogenating catalysts, such as magnesia, or magnesia-zinc oxide, at 500-750°C., chrysene is said to result.[199]

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[195] R. Y. Levina and D. M. Trakhtenberg, *J. Gen. Chem. (U.S.S.R.)*, 1936, 6, 764; *Chem. Abs.*, 1936. 30, 6338; *Brit. Chem. Abs.* A, 1936, 1238.

[196] L. Ruzicka and C. F. Seidel, *Helv. Chim. Acta*, 1936, 19, 424; *Chem. Abs.*, 1936, 30, 6343.

[197] L. Ruzicka and E. Peyer, *Helv. Chim. Acta*, 1935, 18, 676; *Brit. Chem. Abs.* A, 1935, 738; *J. Inst. Pet. Tech.*, 1935, 21, 371A; *Chem. Abs.*, 1935, 29, 5082.

[198] C. D. Nenitzescu and E. Cioranescu, *Ber.*, 1936, 69, 1040; *Chem. Abs.*, 1936, 30, 4824; *Brit. Chem. Abs.* A, 1936, 831.

Aromatic Hydrocarbons

The aromatic hydrocarbons as a class are characterized by high thermal stability. On pyrolysis, they tend to yield more complex aromatic hydrocarbons with the liberation of hydrogen. Rupture of the aromatic ring does appear to take place to some extent, and aliphatic side chains (if present) are usually split off.[200]

Benzene. The statement that the thermal decomposition of benzene is a homogeneous reaction[201] is not substantiated by the kinetic measurements of Mead and Burk,[202] who studied the decomposition at 750 to 852°C. in a silica tube. The heterogeneous nature of the reaction was demonstrated by the increased reactivity when using a tube packed with quartz, but the change in rate was not proportional to the variation in surface. Filling the tube with steel chips caused a larger amount of decomposition than would normally have been expected. The velocity data were accommodated by the equation:

$$kt = \frac{x}{a - x} + 2.3 \log\left(1 - \frac{x}{a}\right)$$

which suggested that this decomposition is a bimolecular surface reaction strongly retarded by the products. The apparent energy of activation is about 50,000 cal. Mead and Burk noted that the materials formed consisted of hydrogen, acetylene, small amounts of other unsaturated gases and methane, biphenyl, *p*-diphenylbenzene and a few higher condensation products. The ratio of weight of gaseous products to weight of solids lessened with increasing partial pressure of benzene at a given temperature but carbon deposition was slight even at 850°C.

The production of biphenyl by pyrolysis of benzene is of technical interest.[203] The yield may be increased by the use of elevated pressures, amounting to about 4 to 5 per cent at 440-450°C. under 170 atmospheres pressure.[204] Catalysts such as nickel and iodine are favorable, a concentration of 6 per cent of the latter giving a 14-17 per cent conversion at 420-440°C. and 125 atmospheres. Iron and nickel are said to be superior to brass, aluminum, copper and chromium for this reaction at 470°C., a 0.5 per cent conversion being obtained with the first two.[205] High pressures of hydrogen inhibit the reaction. In no case was hydrobiphenyl detected, but the deposition of soot shows that some carbonization was undergone as a result of the catalytic action of these metals.

Other Aromatic Hydrocarbons. The results of Pease and Morton[206] indicate that the lower aromatic hydrocarbons may be listed in the following order of decreasing thermal stability at 630°C.: *o*-xylene, toluene, benzene, *m*-xylene, and ethylbenzene. A study of the decomposition of the latter hydrocarbon from the kinetic standpoint showed the reaction at 540-580°C. to be homogeneous and pseudo-unimolecular.[207] The velocity constants for the dissociation of ethylbenzene in this temperature range can be accommodated by the equation:

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[199] British P. 409,837, 1932 to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1934, 618; *Chem. Abs.*, 1934, **28**, 6160. French P. 761,755, 1934; *Chem. Abs.*, 1934, **28**, 4073.

[200] For a review of the pyrolysis of benzenoid hydrocarbons, consult G. Egloff, B. L. Levinson and H. T. Bollman, "Thermal Reactions of Aromatic Hydrocarbons," Universal Oil Products Co., Chicago, **1934**. See also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**, 87.

[201] R. N. Pease and J. M. Morton, *J.A.C.S.*, 1933, **55**, 3190; *Brit. Chem. Abs.* **A**, 1933, 1017; *Chem. Abs.*, 1933, **27**, 4992.

[202] F. C. Mead, Jr., and R. E. Burk, *Ind. Eng. Chem.*, 1935, **27**, 299; *J. Inst. Pet. Tech.*, 1935, **21**, 290A; *Brit. Chem. Abs.* **B**, 1935, 539; *Chem. Abs.*, 1935, **29**, 2826.

[203] See Chapter 5. Also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. For use of Arochlors (chlorinated biphenyl products), see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**.

[204] J. P. Wibaut, H. M. Romijn and H. D. T. Willink, *Rec. trav. chim.*, 1934, **53**, 584; *Brit. Chem. Abs.* **A**, 1934, 763; *Chem. Abs.*, 1934, **28**, 4725.

[205] G. I. Krasnokutski and M. S. Nemtoz, *J. Gen. Chem. (U. S. S. R.)*, 1934, **4**, 132; *Brit. Chem. Abs.* **A**, 1934, 851; *Chem. Abs.*, 1934, **28**, 5743.

[206] R. N. Pease and J. M. Morton, *loc. cit.*

$$\log_{10} k = 15.01 - \frac{70{,}000}{2.3RT}$$

which is almost identical with the corresponding one for the dissociation of ethane.[208] Examination of the products of decomposition of ethylbenzene at 550-600°C. showed that, at small conversions, hydrogen and styrene[209] are the main products. The gaseous hydrocarbons contained small amounts of lower olefins, methane and ethane. These products are accounted by the following reactions:

$$\begin{array}{lll}
(1)\ C_6H_5C_2H_5 & \longrightarrow & C_6H_5CH{=}CH_2 + H_2 \\
(2)\ C_6H_5C_2H_5 & \longrightarrow & C_6H_6 + C_2H_4 \\
(3)\ 2C_6H_5C_2H_5 & \longrightarrow & C_6H_5CH_2CH_2C_6H_5 + CH_4 \\
(4)\ 2C_6H_5C_2H_5 & \longrightarrow & C_6H_5C_6H_4C_2H_5 + C_2H_6
\end{array}$$

of which the first is thought to be the most important. An 82.7 per cent yield of styrene was obtained by Zal'kind and Bulavsky[210] by passage of ethylbenzene diluted with nitrogen over a catalyst of 10 per cent zinc oxide and 90 per cent alumina at 660-670°C. under a pressure of 10 to 13 mm. With nickel oxide-alumina, however, the decomposition of ethylbenzene follows a different course. Thus with this material at 350°C., Ipatieff and Komarewsky[211] identified hydrogen, methane, ethane, benzene, toluene and naphthalene, but no styrene.

Baddeley and Kenner[212] decomposed *p*-xylene by passing it through a silica tube heated to 800°C. Benzene, toluene, 2,6-dimethylanthracene and a small amount of *m*-xylene were obtained. Under similar conditions, 2,6-dimethylanthracene yielded benzene, toluene, naphthalene and anthracene, but apparently no *m*- or *p*-xylene.

Hurd and Bollman[213] have examined the products of pyrolysis of *o*- and *p*-allyltoluenes at 600-700°C. in a quartz tube. The gas was principally methane with a considerable quantity of hydrogen and olefins, ethylene predominating in the latter. The liquid obtained consisted of toluene, *o*- and *p*-xylene, naphthalene and traces of benzene. The results seem to indicate that alpha bonds are more resistant to heat than the beta bonds. Although 4-phenyl-1-butene is less stable than *o*-allyltoluene, it could not be isomerized to the latter hydrocarbon.

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[207] A pseudo-unimolecular reaction is a special type of decomposition represented by the general equation:

$$A + B \longrightarrow C + D$$

in which the substance B is a catalyst, or is present in high concentration as compared with A, so that its concentration will not change appreciably throughout the experiment, thus giving the effect of a unimolecular reaction. See F. O. Rice and H. C. Urey, "Reaction Velocity in Homogeneous Systems," in H. S. Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York, 1930, 959.

[208] Pease and Morton give the equation

$$\log_{10} k = 15.12 - \frac{73{,}200}{2.3\,RT}$$

[209] See Chapter 5. Also Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[210] Y. S. Zal'kind and G. L. Bulavsky, *Plasticheskie Massui*, 1935, (3), 9; *Chem. Abs.*, 1936, **30**, 1368.

[211] V. N. Ipatieff and V. I. Komarewsky, *J.A.C.S.*, 1936, **58**, 922; *Brit. Chem. Abs.* **A**, 1936, 975; *Chem. Abs.*, 1936, **30**, 5189; *J. Inst. Pet. Tech.*, 1936. **22**, 395A.

[212] G. Baddeley and J. Kenner, *Ber.*, 1936, **69**, 902; *Brit. Chem. Abs.* **A**, 1936, 714; *Chem. Abs.*, 1936. **30**, 4461.

[213] C. D. Hurd and H. T. Bollman, *J.A.C.S.*, 1934, **56**, 447; *Brit. Chem. Abs.* **A**, 1934, 398; *J. Inst. Pet. Tech.*, 1934, **20**, 240A; *Chem. Abs.*, 1934, **28**, 1669.

Chapter 3

Cracking Processes and Some of Their Products

The term "cracking" is commonly used to denote the conversion of petroleum fractions to motor fuels through the application of heat and pressure.[1] The production of optimum yields of high grade gasoline from various crudes or their fractions is the aim of practically all of these operations, although there are exceptions to this generalization.[2] Egloff, Crandal and Doty[3] remind us that kerosene, gas oil, fuel oil, tractor fuel, furnace oil, Diesel oil, road oil, asphalt and high grade coke may also be produced in these operations. According to Auld[4] cracking is not only a method for augmenting the proportion of gasoline obtainable from crude oil, but it is "one of the most important means we have for adjusting the yields of the various products of petroleum to meet the ever-changing demands of the market."

Investigations in the field of cracked gasoline have been promoted largely by the demands for 100-octane fuel desired by the aviation and automotive industries. As a result, isooctane, which formerly cost $20 a gallon and was used only for the standardization of the antiknock ratings of secondary fuels, is now being produced in substantial quantities at a comparatively low price level. The effect of this development is shown not only in the increase in automobile top speed from 60 miles per hour in 1925 to over 100 in 1936, and in the cruising speed of airplanes from 80 to 260 miles per hour over the same period, but also in the gain in power output of 20 to 30 per cent for 100-octane fuel over 87-octane commercial gasoline. The latter fact is important in the field of aviation as this reduction in fuel consumption permits the transportation of larger pay loads.[5] The enormous scale on which the cracking industry is conducted has also led to the production of another type of motor fuel, "polymer gasoline," which is prepared from cracking gases. A discussion of this topic will be considered subsequently under polymerization.[6]

The importance of cracked gasoline can be readily ascertained from Table 28,

TABLE 28.—*Production of Motor Fuel in the United States in Thousands of Barrels (42 gallons) and Per Cent of Total.*

	1933		1934		1935	
	Barrels	Per Cent	Barrels	Per Cent	Barrels	Per Cent
Straight run	195,622	48.2	206,337	49.5	219,583	48.0
Cracked	180,623	44.4	182,433	43.8	207,537	45.3
Natural Gasoline	30,319	7.4	28,162	6.7	30,572	6.7
Total	406,564		416,932		457,692	
Daily Average	1,113		1,142		1,254	

[1] P. C. Keith and W. B. Montgomery, *Ind. Eng. Chem.*, 1934, **26**, 190; *Chem. Abs.*, 1934, **28**, 1848; *Brit. Chem. Abs.* B, 1934, 438; *J. Inst. Pet. Tech.*, 1934, **20**, 179A.

[2] See Chapters 4, 5 and 7 for the production of olefins, aromatics and hydrogen and carbon, respectively.

[3] G. Egloff, E. E. Crandal and M. M. Doty, "The Cracking Art in 1935," Universal Oil Products Co., Chicago, 1936. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[4] S. J. M. Auld, "Cracking," in "Petroleum, Twenty-Five Years Retrospect, 1910-1935," The Institution of Petroleum Technologists, London, 1935, 86.

[5] G. Egloff, E. E. Crandal and M. M. Doty, *loc. cit.*

[6] See Chapter 26.

which shows the production of motor fuel from the three major sources in the United States during 1933, 1934 and 1935. The quantity of cracked fuel amounts to approximately 44 per cent of the total output, and is just slightly under the production of the straight run fuel.[6a] However, in 1934 the cracking processes led to a conservation of 792 million barrels of crude oil, or 46.92 per cent of the total crude oil consumed.[6b] In this respect, a 13.7 per cent increase in the output of cracked gasoline during 1935 as compared with 1934 is noteworthy.

TABLE 29.—*Distribution of the Cracking Capacity of the World, 1935.*

Country	Number of Refineries	Daily Crude Oil Capacity Barrels	Refineries with Cracking Plants	Daily Cracking Capacity Barrels
Argentina	16	80,000	8	34,050
Australia	3	5,100	1	800
Austria	8	8,150	—	—
Bahrein Island	1	10,000	—	—
Belgium	7	7,625	3	2,300
Belgium Congo	1	250	1	150
Bolivia	2	400	—	—
Canada	42	159,400	14	73,150
Canary Islands	1	5,000	1	2,000
Chile	2	475	—	—
Colombia	1	9,000	—	—
Cuba	1	5,000	1	1,800
Czechoslovakia	11	10,225	1	1,100
Ecuador	3	850	—	—
Egypt	2	11,500	1	2,000
France	17	122,550	14	55,950
Germany	29	46,000	4	8,000
Hungary	4	6,600	—	—
India	7	34,500	3	6,600
Iran (Persia)	2	168,000	1	65,500
Iraq	2	2,500	—	—
Italy	9	34,000	4	10,700
Japan	13	28,800	7	8,000
Latvia	1	200	—	—
Manchukuo	2	6,000	1	850
Mexico	8	106,300	3	17,000
Netherlands	1	10,000	1	9,000
Netherlands (Dutch)				
East Indies	9	137,500	3	26,000
West Indies	3	350,000	3	98,000
Norway	1	1,000	—	—
Peru	2	17,000	1	6,800
Poland	16	20,750	2	2,000
Rumania	42	240,050	7	35,850
Spain	1	1,500	—	—
Sweden	1	1,200	1	600
Trinidad	5	39,500	1	10,000
Union of South Africa	1	1,000	—	—
U. S. S. R.	10	517,300	7	65,500
United Kingdom	13	78,600	4	11,500
United States	496	3,815,470	211	2,095,521
Uruguay	1	5,000	1	1,200
Venezuela	6	25,000	—	—
Yugoslavia	2	3,400	1	1,000
Total	805	6,132,695	311	2,652,921

The above table includes plants under construction.

[6a] G. R. Hopkins and A. B. Coons, Statistical Appendix, Minerals Yearbook, 1934, 243; 1935, 404. A. G. White, G. R. Hopkins and H. A. Breakey, Minerals Yearbook, 1936, 715, U. S. Government Printing Office, Washington.

[6b] G. Egloff, E. E. Crandal and M. M. Doty, *loc. cit.* See also *Oil & Gas J.*, 1936, 34 (35), 22.

Although the United States produces almost 80 per cent of the total world supply of cracked gasoline, the advances made in other countries during 1935 were quite significant, according to Egloff, Crandal and Doty. They summarize the reasons for the increased capacity in other countries as: (1) refiners have realized that balanced operation necessitates the inclusion of cracking, (2) the demand for motor fuel is constantly increasing and (3) higher antiknock-rating fuels are desired. The distribution of the cracking capacity of the world is shown in Table 29. It will be seen that the output of the Dutch West Indies (which ranks second) is less than 4 per cent of the total, or about one-twentieth of that of the United States. Canada, Russia, Iran (Persia), France and Argentina are the only other important producers, and their total is only about 11 per cent of the figure for the world.

Egloff and Nelson[7] have pointed out that the cracking processes employed during 1935-6 are highly flexible in their application. Due to the introduction of multiple heating coils, different time-temperature-pressure conditions dependent upon the nature of the cracking stock are possible. Furthermore, these are not limited to the production of gasoline. A large variety of liquid fuels, ranging from kerosene to fuel oil, can be made, depending upon the operating conditions.[8] Whereas in 1913 cracking runs of 2 days' duration were considered maximal, units now in use are capable of operating continuously over spans of more than 150 days.

The Thermodynamics of Cracking[8a]

A study of the thermodynamics of cracking leads to several interesting conclusions. Considering the thermal cleavage of the members of the paraffin series, two types of reaction are possible: dehydrogenation and true chain rupture. Schultze[9] has represented the variation of free energy change with temperature and composition for these two types of reaction (under equilibrium conditions) by the equations,

(1) $$C_nH_{2n+2} = C_nH_{2n} + H_2; \quad \Delta F = 33400 - 27.9T - (500 + T)n$$

and

(2) $$C_{(m+n)}H_{2(m+n)+2} = C_mH_{2m+2} + C_nH_{2n}; \quad \Delta F = 18700 - 26.9T - (500 + T)n$$

In order for reaction (1) to take place at 400°C. (673°K.), that is, to give negative value for the free energy change, the molecules must be of the size of dodecane ($n = 12$) or tridecane ($n = 13$). Similarly, dehydrogenation of heptane to heptene should occur only at temperatures in excess of 600°C. On the other hand, reaction (2) is thermodynamically possible for all paraffins above propane at the temperatures encountered in commercial cracking (390-630°C.) and is much the more probable of the two. The peculiarity of the latter reaction is that only the size of the olefin molecule produced and the temperature are decisive for evaluating the free energy change in this case. However, even the most improbable case, involving the formation of a large paraffin molecule along with a small olefin molecule, is thermodynamically more favored than dehydrogenation according to equation (1). In addition, it will be noted that there are several possibilities as to the nature of the decomposition into complementary olefins and paraffins, as given

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[7] G. Egloff and E. F. Nelson, *Oil & Gas J.*, 1936, **35** (6), 50; (7), 34; (8), 43; *Chem. Abs.*, 1936, **30**, 7828; *J. Inst. Pet. Tech.*, 1936, **22**, 446A, 447A, 504A. *Chem. Eng. Cong. World Power Conf.*, 1936, **C13**, 1; *Brit. Chem. Abs.* **B**, 1936, 774. Also "The Modern Cracking Process," Universal Oil Products Co., Chicago, 1936.

[8] Reviews on cracking processes have been given by: G. Egloff and E. E. Crandal, *J. Inst. Pet. Tech.*, 1935, **21**, 334; *J. Inst. Pet. Tech.*, 1935, **21**, 304A; *Chem. Abs.*, 1935, **29**, 4928. G. Egloff and B. L. Levinson, *J. Inst. Pet. Tech.*, 1934, **20**, 343; *J. Inst. Pet. Tech.*, 1934, **20**, 414A; *Chem. Abs.*, 1934, **28**, 4581. P. C. Keith and W. B. Montgomery, *Ind. Eng. Chem.*, 1934, **26**, 190; *Chem. Abs.*, 1934, **28**, 1848; *Brit. Chem. Abs.* **B**, 1934, 438; *J. Inst. Pet. Tech.*, 1934, **20**, 179A. R. Fussteig, *Mat. grasses*, 1934, **26**, 10295; 1935, **27**, 10380, 10465; *Chem. Abs.*, 1935, **29**, 3815; 1936, **30**, 1547. F. Rosendahl, *Asphalt Teer Strassenbautech.*, 1934, **34**, 217; *Chem. Abs.*, 1935, **29**, 1615. I. Siftar, *Arhiv. Hem. Farm.*, 1934, **8**, 121; *Chem. Abs.*, 1934, **28**, 5971. A. Sachanen, *Chim. & ind.*, 1934, **31**, 32; *Brit. Chem. Abs.* **B**, 1934, 308; *Chem. Abs.*, 1934, **28**, 3879.

[8a] For a discussion of thermodynamics and its application to petroleum technology, see Chapter 54.

[9] G. R. Schultze, *Angew. Chem.*, 1935, **48**, 567; 1936, **49**, 268; *J. Inst. Pet. Tech.*, 1935, **21**, 413A; *Chem. Abs.*, 1936, **30**, 6175; *Brit. Chem. Abs.* **B**, 1936, 535. Also *Oel, Kohle, Erdoel, Teer*, 1936, **12**, 267; *Chem. Abs.*, 1936, **30**, 6175; *Brit. Chem. Abs.* **B**, 1936, 535. *Z. Elektrochem.*, 1936, **42**, 674; *Brit. Chem. Abs.* **B**, 1936, 1138; *Chem. Abs.*, 1936, **30**, 8587. See also Chapter 54.

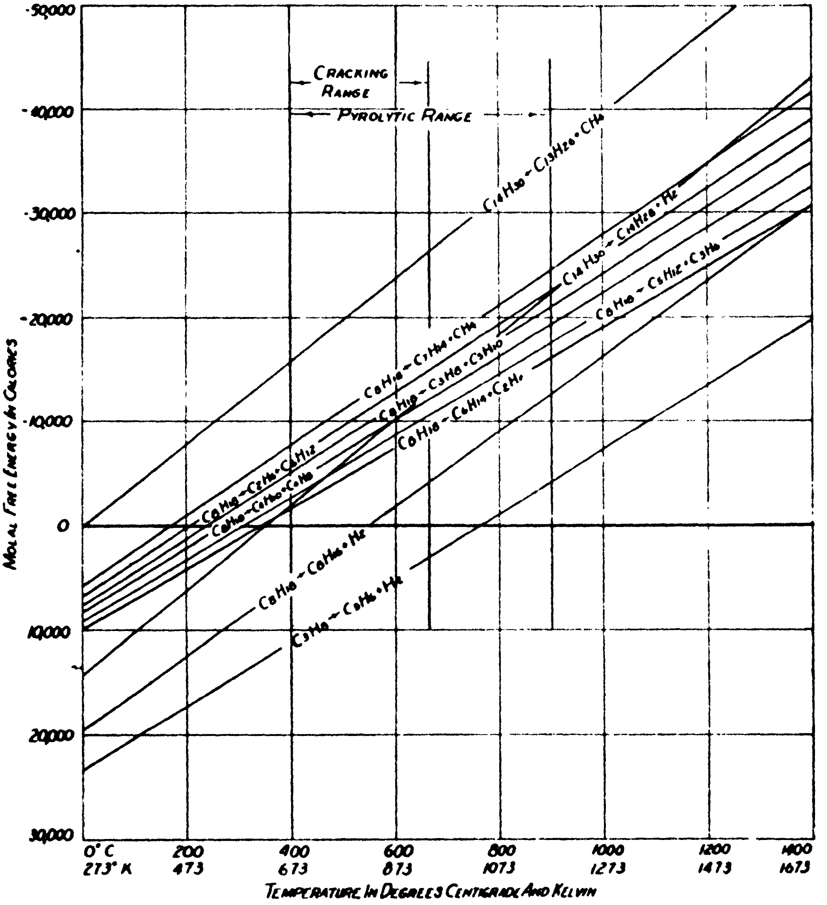

FIG. 26.—Variation of Molal Free Energy with Temperature for Typical Cracking Reactions.

by the expression $(m + n - 2)$. The limiting case for the dissociation is when m is equal to unity (corresponding to methane).

Fig. 26 is a graphical representation of equations (1) and (2) using tetradecane ($C_{14}H_{30}$), octane and propane as examples. In the ordinary range of temperatures used in commercial cracking (390-630°C.) the ΔF values obtained from equation (2) for the decomposition of tetradecane to methane and tridecene and of octane (all six possibilities of this hydrocarbon) are decidedly negative, indicating that all paraffins higher than heptane or octane will readily tend to crack to lower molecular weight products. Dehydrogenation of tetradecane is also possible, but that of octane is quite improbable except at temperatures above 600°C. Under these conditions, propane should not be expected to undergo dehydrogenation but will break down to give methane and ethylene. However, at temperatures of about 900°C., such as those encountered in pyrolysis, dehydrogenation of these paraffins (especially the higher molecular weight members of the series) does become a prominent type of decomposition, although the thermodynamic tendency is still not as high as that for the rupture of the chain.[9a]

Demethylation, that is, the case in which the olefin resulting from the rupture of the original molecule is as large as possible, is the type of splitting best favored thermodynamically. This theoretical conclusion tends to be confirmed by the presence of methane as the major ingredient of cracking gases. According to Schultze such deductions are in complete agreement with Haber's cracking rule,[10] which states that of the two molecules formed in the cleavage of a paraffin, the smaller should be paraffinic and the larger olefinic. However, the differences in the free energy changes for the various possibilities for the fracture of a molecule (at a given temperature) are so small that by the application of pressure the breaking point in the molecule may be shifted. Following LeChatelier's principle, the application of pressure should favor the formation of products having the lowest vapor tension. In this case the resultants would be those compounds formed by central fracture.

Schultze has also demonstrated the impossibility of the immediate formation of condensation products from paraffins according to the reaction:

$$\mathrm{mC_nH_{2n+2} = C_{mn}H_{2mn+2} + (m-1)H_2;} \quad \Delta F = (m-1)(14{,}700 - T)$$

This reaction is unfeasible at any temperature. When condensation products are formed, Schultze believes that they result indirectly from the decomposition of olefins.

The dimerization of olefins according to the scheme:

$$\mathrm{2C_nH_{2n} = C_{2n}H_{4n};} \quad \Delta F = -18{,}700 + 26.9T$$

is interesting because, as the first approximation, the free energy is independent of the size of the olefin molecule. Above 425°C., however, depolymerization occurs, but this tendency for decomposition may be retarded by the application of pressure. Likewise, disproportionation according to the equation:

$$\mathrm{C_{m+n}H_{2(m+n)} = C_mH_{2m+2} + C_nH_{2n-2};} \quad \Delta F = 34500 - 33.7T + (500 - T)n$$

yielding one molecule of a paraffin and one of an acetylene hydrocarbon, is probable at temperatures above 800°C., in the case of propane. Similarly, the formation of naphthenes by condensation of ethylene is quite likely at low temperatures, especially under high pressure.[11]

According to Parks and Huffman,[12] at temperatures below 500°K. (237°C.) paraffins and cycloparaffins are more stable than olefins and aromatics. At higher temperatures, however, this stability is reversed and olefins and aromatics become the more permanent hydrocarbons. Thus, Schultze[13] shows that the dehydrogenation of cyclohexane to benzene should be expected at temperatures above 200°C. In both cycloparaffin and aromatic hydrocarbons having long side chains, the tendency is towards splitting off the chain rather than rupturing the ring.

[9a] It should be borne in mind that such high temperatures, though attainable in the laboratory, are not employed in commercial cracking operations.

[10] F. Haber, *Ber.*, 1896, 29, 2691; *J.C.S.*, 1897, 72 (1), 133; *Chem. Zentr.*, 1897, 1, 86.

[11] See Chapter 54.

[12] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, 1932.

[13] G. R. Schultze, *loc. cit.*

KINETICS OF THE CRACKING PROCESS

In the early stages of reaction and at small percentage decomposition, cracking of pure hydrocarbons and also petroleum fractions follows a unimolecular law. However, at more pronounced cracking, secondary reactions, involving the interaction of the primary products, proceed to a marked extent. Many of the latter reactions and also the dimerization of olefins are of a bimolecular nature.[14] This fact greatly complicates a study of the rates of reaction. Dintzes, Eshevskaya and Klabina[15] have reported that the velocity of the cracking reaction is practically independent of the degree of cracking or duration of the reaction, provided the percentage decomposition is kept small. Their experiments were carried out with various petroleum fractions, using a vapor-phase cracking system. The extent of decomposition in all cases was limited to 10 or 15 per cent.

The influence of temperature on the velocity of the cracking reaction is expressed by the integrated form of the Arrhenius equation,

$$\log_e K = \frac{-E}{RT} - C$$

where K is the monomolecular velocity constant, E is the energy of activation, R, the gas constant (1.985 cal. per degree), T, the absolute temperature (°K.), and C is the integration constant. (The important physico-chemical constant, E, the activation energy of the reaction, must be clearly differentiated from the heat of reaction.) The energies of activation of a wide variety of pure hydrocarbons[16] and of various petroleum fractions in both liquid and vapor phase processes have been determined, and although these values may be fairly close to one another, they are by no means identical.

For the formation of gas, gasoline and coke from gas oil, Geniesse and Reuter[17] found a value of E equal to 53,400 cal. On the other hand, Keith, Ward and Rubin[18] obtained 57,100 cal. for E, considering only the formation of gas and gasoline. Huntington and Brown[19] report values of E and C of 59,200 cal. and 32.55, respectively, for the commercial production of gas, gasoline and coke from a feed stock containing 75 per cent of recycle material, and having an A.P.I. gravity of 24.8 at 60°F. A critical review of this question has been contributed by Obryadchikov[20] who concludes that the energy of activation is higher for light products and lower for heavier ones. He also states that aromatic fractions require a higher degree of activation than paraffins of the same molecular weight. The activation energy of cracked naphtha is lower than that of straight-run naphtha. However, this condition is reversed for heavier hydrocarbon fractions.

The actual data for E are higher when gasoline is taken as the sole product than when all the decomposition products are included in the calculation.[21] The temperature coefficients of cracking velocity are naturally in the reverse order of the activation energies, being lower for the lighter fractions than for the heavier ones and also lower for aromatic charging stocks than for paraffinic ones. A value of $E = 65{,}800$ cal. per mole has been found by Lederer[22] for the cracking of a paraffin base oil at 450°C. and of mazout at 425°C.

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[14] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934, for a discussion of the Physical Chemistry of the Cracking Process.

[15] A. I. Dintzes, M. P. Eshevskaya and T. I. Klabina, *Khim. Tverdogo Topliva*, 1935, 6, 428; *Chem. Abs.*, 1935, **29**, 7623; *J. Inst. Pet. Tech.*, 1936, **22**, 95A; *Brit. Chem. Abs.* **B**, 1937, 108.

[16] See Chapters 2 and 54.

[17] J. C. Geniesse and R. Reuter, *Ind. Eng. Chem.*, 1930, **22**, 1274; *Brit. Chem. Abs.* **B**, 1931, 327; *Chem. Abs.*, 1931, **25**, 1368.

[18] P. C. Keith, J. T. Ward and L. C. Rubin, *Proc. Amer. Pet. Inst.*, 1933, **14** (3), 49; *J. Inst. Pet. Tech.*, 1934, **20**, 95A.

[19] R. L. Huntington and G. G. Brown, *Ind. Eng. Chem.*, 1935, **27**, 699; *Chem. Abs.*, 1935, **29**, 5257; *Brit. Chem. Abs.* **B**, 1935, 709.

[20] S. N. Obryadchikov, *Neft. Khoz.*, 1934, **26** (12), 35; *Brit. Chem. Abs.* **B**, 1936, 402; *Chem. Abs.*, 1935, **29**, 4926.

[21] S. N. Obryadchikov and S. Heiman, *Neft. Khoz.*, 1935, **29** (10), 60; *J. Inst. Pet. Tech.*, 1936, **22**, 148A; *Chem. Abs.*, 1936, **30**, 3985.

On the basis of experiments with various hydrocarbons, Pease and Morton[23] suggested that the ratio of the energy of activation to the integration constant of the Arrhenius equation was a constant. This view has been discussed by Dintzes, Eshevskaya and Klabina[24] who found that the values of the ratio varied from 4.16 to 4.94. These same investigators report that individual narrow cuts of straight-run Grozny and Baku petroleums of boiling ranges 100-270°C. are characterized by activation energies varying between 46,000 to 54,000 cal.

In general, the cracking process is decidedly endothermic, although certain of the reactions involved, such as polymerization, are actually exothermic. On account of its complex nature, the heat of reaction of a cracking operation depends greatly upon the degree of cracking as well as upon the character of the charging stock. In this respect, Butkov and Chechkina[25] have stated that when cracking a Baku kerosene distillate feed at 20°C., the following heat input is required: 941-944 cal. per kg. if cracked at 625°C., 1052-1095 cal. at 675°C. and 1284-1337 cal. at 725°C.

FUNDAMENTAL FACTORS INFLUENCING CRACKING

The fundamental variables in all types of cracking operations are temperature, time of reaction, pressure and the character of the charging stock. Although catalysts naturally affect the velocity and course of cracking, their influences are generally of secondary importance. This topic will be considered subsequently in this chapter. In addition to the four variables mentioned above, it is necessary in industrial operations (involving recycling) to specify another factor, the conversion per pass, or the extent to which the reactions are allowed to proceed before the products are separated from the cycle stock which is returned to the system. Although this quantity is a function of the other variables, its influence on the characteristics of the operation is best considered independently.[26]

Temperature variations affect both the velocity of the cracking reaction and also the nature of the hydrocarbons formed. Thus, high-temperature (1000°F.) treatment results in high olefin and aromatic content liquids. On the other hand low-temperature (750-850°F.) cracking furnishes principally paraffinic and naphthenic hydrocarbons.

The velocity of cracking depends markedly upon the temperature of the reaction. Expressing the rate of change of the velocity with respect to temperature by the Arrhenius equation and integrating between temperature limits gives the relation:

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[22] E. L. Lederer, *Petroleum Z.*, 1935, **31** (12), 1; *J. Inst. Pet. Tech.*, 1935, **21**, 167A; *Chem. Abs.*, 1935, **29**, 7624; *Brit. Chem. Abs.* B, 1935, 581.

[23] R. N. Pease and J. M. Morton, *J.A.C.S.*, 1933, **55**, 3190; *Chem. Abs.*, 1933, **27**, 4992; *Brit. Chem. Abs.* A, 1933, 1017.

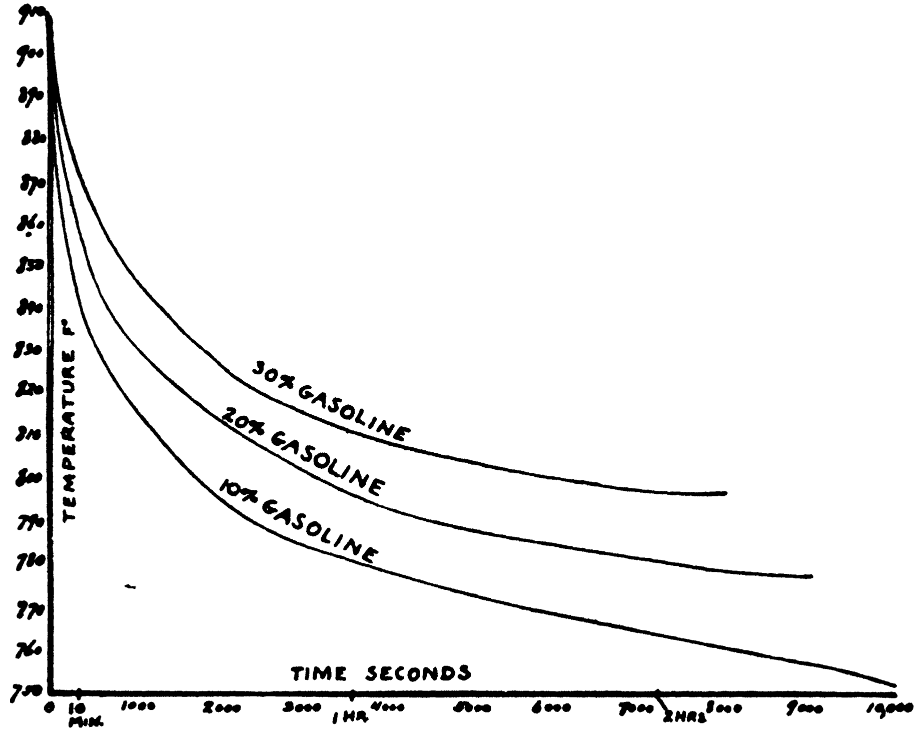
[24] A. I. Dintzes, M. P. Eshevskaya and T. I. Klabina, *loc. cit.*

[25] N. A. Butkov and O. M. Chechkina, *Neft. Khoz.*, 1933, **25**, 92; *Chem. Abs.*, 1934, **28**, 3227; *Brit. Chem. Abs.* B, 1934, 820; *J. Inst. Pet. Tech.*, 1934, **20**, 413A.

[26] Reviews on the influence of these factors have been given by H. Sydnor, *Ind. Eng. Chem.*, 1934, **26**, 184; *Chem. Abs.*, 1934, **28**, 1849; *Brit. Chem. Abs.* B, 1934, 438; *J. Inst. Pet. Tech.*, 1934, **20**, 158A. A. W. Trusty, *Nat. Pet. News*, 1935, **27** (45), 34; *Chem. Abs.*, 1936, **30**, 2734. G. G. Brown, W. K. Lewis and H. C. Weber, *Ind. Eng. Chem.*, 1934, **26**, 325; *Brit. Chem. Abs.* B, 1934, 486; *J. Inst. Pet. Tech.*, 1934, **20**, 234A; *Chem. Abs.*, 1934, **28**, 3567. A. I. Dintzes, *Uspekhi Khim.*, 1934, **3**, 936; *Chem. Abs.*, 1935, **29**, 6743. A. Sachanen, *Erdöl u. Teer*, 1934, **10**, 105; *Chem. Abs.*, 1934, **28**, 7499; *Brit. Chem. Abs.* B, 1935, 7; *J. Inst. Pet. Tech.*, 1934, **20**, 412A. H. Otsuka, *J. Fuel Soc. Japan*, 1936, **15**, 59; *Brit. Chem. Abs.* B, 1936, 818. E. G. Ginzburg, S. N. Popov and T. V. Prokof'ev, *Aserb. Neft. Khoz.*, 1935 (10-11), 73; *Chem. Abs.*, 1936, **30**, 8587. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

$$\log_e \frac{k_2}{k_1} = \frac{E}{R}\left(\frac{T_2 - T_1}{T_2 T_1}\right)$$

where k_1 and k_2 are the velocity constants at the absolute temperatures T_1 and T_2, respectively, E is the energy of activation in calories, and R is the gas constant (1.985 cal. per °K.). For an increase of 10°C. (18°F.) the velocity constant is doubled at room temperatures. However, at the temperatures encountered in cracking, this approximation is often not very accurate. Egloff and Nelson[27] report that the rate is doubled by a rise of 21°F. at 800°F. and 26°F. at 900-950°F. The variation of cracking velocity with temperature is also dependent upon the character of the charging stock. In general, lighter fractions have lower temperature coefficients than the heavier fractions, so that a smaller increase in temperature is sufficient to double the reaction velocity in the former case. Obryadchikov[28]



Courtesy National Petroleum News

FIG. 26A.—Effect of Time and Temperature on Gasoline Yields in Cracking Crude Oils. (A. W. Trusty)

reported that in reforming[29] of a gasoline, requiring an activation energy of 70,000 cal. per mole, at 400°C. the reaction will be doubled for a 9°C. rise in temperature, and at 500°C., for a 12°C. rise.

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[27] G. Egloff and E. F. Nelson, *Oil & Gas J.*, 1936, 35 (6), 50; (7), 34; (8), 43; *Chem. Abs.*, 1936, 30, 7878; *J. Inst. Pet. Tech.*, 1936, 22, 446A, 447A, 504A. *Chem. Eng. Cong. World Power Conf.*, 1936, C18, 1; *Brit. Chem. Abs.* B, 1936, 774.

[28] S. N. Obryadchikov, *Neft. Khoz.*, 1934, 26 (12), 35; *Brit. Chem. Abs.* B, 1936, 402; *Chem. Abs.*, 1935, 29, 4926.

The effect of temperature and time in cracking gas oil has been discussed by Trusty.[30] At about 800°F., a 10 per cent yield of gasoline is obtained with a heating time of 30 minutes, but at 890°F. this may be accomplished in 10 seconds. Similarly, to form 30 per cent gasoline at 800°F. requires about 2 hours heating, yet at 890°F. the time is reduced to less than 3 minutes.

In commercial cracking units, the time element varies considerably. High temperature operation (say at 1100°F.), as exemplified by the Gyro vapor-phase unit, is usually carried out with heating times of 1 to 2 seconds. Vapor-phase processes operating at 825°F. ordinarily employ an average of 15 to 20 minutes for an 18 per cent yield of gasoline, according to Trusty.[31] However, for mixed-phase processes at 900°F., the same conversion is obtained in 1.5 to 2 minutes. On the other hand, with low temperature operation (about 820°F.), as with the Cross, Dubbs or Tube and Tank units, the reaction time is generally in the magnitude of 20 minutes and may even be as long as 6 hours.

Geniesse and Reuter[32] have shown that the influence of both time and temperature on the yields of cracked products (i.e., the conversion per pass) may be expressed as a composite variable, termed the "time-temperature index." Arbitrarily taking 480°C. as the standard cracking temperature, and assuming that the rate of cracking is doubled for a 17°C. rise, the time-temperature index, Θ, is given by the relation:

$$\Theta = 2^{x}t$$

where $x = \dfrac{T - 480}{17}$, T is the cracking temperature, °C., and t is the time of contact in minutes. For a given charging stock the extent of cracking is approximately the same for a given value of the time-temperature index. In effect, this means that analogous results may be obtained by cracking at low temperatures with long contact, or at higher temperatures in corresponding shorter heating times. On the basis of this index, Turner and LeRoi[33] have correlated octane number improvement in naphtha reforming under high pressures at temperatures up to 1025°F. These investigators used approximately the same reference temperature, 900°F. (482°C.), however they assumed that the velocity of reaction doubles for a 25°F. rise in temperature. The corresponding value of x in this case is

$$x = \frac{T - 900}{25}$$

where T is the temperature in °F. From experimental data obtained in reforming both straight run and cracked naphtha in a Tube and Tank unit, these investigators arrived at an empirical relation between the octane number and Θ (the equivalent seconds at 900°F.) as shown in Fig. 27. Thus, if it was desired to improve the octane number of a naphtha from 60 to 70 by reforming, the time necessary for the operation was estimated from this chart by taking the difference between the abscissae corresponding to the above octane number ordinates (that is, 560 — 200 = 360 seconds, required in this case). The average deviation from these values was found to be about 1 octane number. Turner and LeRoi state that variations in pressure, temperature and charging rate exerted no apparent influence on the results. In their opinion, equivalent time[34] is the decisive factor in determining the detonating quality of the reformed gasoline.

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[29] The term "reforming" is used to denote the cracking of naphthas and low grade gasolines to produce higher octane number motor fuels.

[30] A. W. Trusty, *Nat. Pet. News*, 1935, 27 (45), 34; *Chem. Abs.*, 1936, 30, 2734.

[31] A. W. Trusty, *Nat. Pet. News*, 1935, 27 (45), 34; *Chem. Abs.*, 1936, 30, 2734.

[32] J. C. Geniesse and R. Reuter, *loc. cit.* See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[33] S. D. Turner and E. J. LeRoi, *Ind. Eng. Chem.*, 1935, 27, 1347; *Chem. Abs.*, 1936, 30, 275; *J. Inst. Pet. Tech.*, 1936, 22, 20A; *Brit. Chem. Abs.* B, 1936, 178; *Nat. Pet. News*, 1935, 27 (24), 30; *J. Inst. Pet. Tech.*, 1935, 21, 339A.

The results of Schutt[35] on the influence of various factors on the vapor-phase cracking of oils indicated that the ratio of gas to gasoline in the products could not be correlated with the time-temperature index. The octane number of the product was a function of the temperature, but was not particularly related to the time factor or recycle rate. The temperature was also considered by Sydnor[36] to be the controlling factor for determining the octane number in mixed phase cracking at 860-900°F. under 200 lbs. per sq. in. pressure. On the other hand, Keith, Ward and Rubin[37] concluded that the temperature had apparently no effect on the octane number but that the latter was closely related to the conversion per pass.

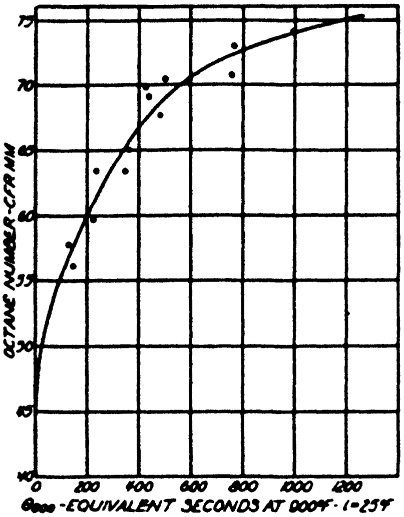

FIG. 27.
Correlation of Octane Numbers with Cracking Conditions. (S. D. Turner and E. J. Le Roi)

Courtesy Industrial and Engineering Chemistry

Pressure. Sachanen and Tilicheyev[38] reported that pressure has no substantial influence on either cracking or on the character of the product obtained. The primary reaction taking place during the destruction of the hydrocarbon chain is of a monomolecular type, consequently the application of pressure (i.e., the concentration of the reacting molecules in the reacting zone) should not affect its velocity. Nemtzov,[39] however, does not agree with the above conclusions of

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[34] In this case, the term "equivalent time" refers to the amount of time (in seconds) required at 900° F., which may be obtained from the time-temperature curve on the assumption that the cracking rate doubles with a 25° F. rise in temperature.

[35] H. C. Schutt, *Amer. Pet. Inst. Proc. 14th Annual Meeting*, 1933, Sec. III, 132; *Chem. Abs.*, 1934, 28, 3879.

[36] H. Sydnor, *loc. cit.*

[37] P. C. Keith, J. T. Ward and L. C. Rubin, *Proc. Amer. Pet. Inst.*, 1933, 14 (3), 49; *J. Inst. Pet. Tech.*, 1934, 20, 95A.

[38] A. N. Sachanen and M. D. Tilicheyev, "Chemistry and Technology of Cracking." The Chemical Catalog Co., Inc., New York, 1932.

[39] M. S. Nemtzov, *J. Inst. Pet. Tech.*, 1935, 21, 644; *J. Inst. Pet. Tech.*, 1935, 21, 375A; *Brit. Chem. Abs.* B, 1935, 836; *Chem. Abs.*, 1935, 29, 6410.

Sachanen and Tilicheyev. From the results of high pressure cracking experiments, he states that not only the character of the resultants but also the reaction velocity is dependent upon the pressure. The olefins formed in the cracking operation have a tendency to polymerize, and since polymerization reactions are bimolecular, they will be favored by the application of high pressure. For instance, in the case of simple dimerization the rate of the reaction is proportional to the concentration of the reacting molecules and, therefore, the square of the pressure. Because of this fact, the products obtained by cracking under high pressures should contain much larger proportions of polymerized olefins than the corresponding low pressure treatments.

One direct effect of pressure, according to Nemtzov,[40] is the increased yields of gasoline in place of gases. The suppression of gas formation by higher pressures is in accordance with the observations of Keith, Ward and Rubin, who found that the gas yield varied inversely as the pressure.[41] Their conclusions were based on data obtained by cracking gas oil at 800-1100°F. under pressures of 100 to 1000 lbs. per sq. in.

That the pressure exerts a considerable influence on the character of the product has also been noted by Trusty.[42] The readily condensable hydrocarbons, particularly the diolefins, are polymerized under pressure and are eliminated from the gasoline in the form of high-boiling heavy residues. The stability of the liquid products, with respect to gum formation, is thus greatly increased. As an example, gas oil cracked at 1075°F. under 15 lbs. per sq. in. pressure resulted in a gasoline with a gum content of 600 mg. per 100 cc. (copper dish method), whereas, when operating under 100 lbs. per sq. in. at the same temperature, the gum value was reduced to 100 mg. per 100 cc.

Sydnor[43] observed that distinctly higher yields of gasoline are obtained at low than at higher pressure for operations carried out at the same temperature. The data obtained in his experiments with a Mid-Continent gas oil of 33.7° A.P.I. gravity, using a Tube and Tank unit, are given in Table 30. Both at 860 and 900°F. conversion to gasoline was decreased about 10 per cent by an increase in pressure from 200 to 750 lbs. per sq. in. However, the formation of gas and coke was decreased by the application of higher pressures.

TABLE 30.—*Effect of Pressure on Cracking Gas Oil Using Tube and Tank Unit.*

Pressure, lbs. per sq. in.	200	200	200	750	750	750	750
Reaction temperature, °F.	860	900	900	860	860	900	900
Conversion per pass, %	7.5	7.5	20	7.5	20	7.5	20
Gasoline, 400°F.E.P., %	69.3	67	62	63	59.5	61.5	57.9
Fuel oil, 12°A.P.I., %	24	27	23.4	30	32.4	29.6	32
Gas and coke, %	13.2	11.6	20	11.4	12.2	12.6	13.4
Octane number of gasoline, CFR. method	63.5	69	69	—	—	67	69.6

Trusty[44] has summarized the advantages of the use of pressure as (1) better conditions for heat transfer, (2) absence of local overheating and (3) increased yield of gasoline products.[45]

Character of Charging Stock. The character of the charging stock is of much greater importance in influencing the yields of products of mixed-phase rather than of vapor-phase cracking. In the case of vapor-phase treatment, Trusty states that the character of the charging stock has no effect. Wagner,[46] however, disagrees with this observation on the basis of data obtained by vapor-phase cracking at 1100°F. and low pressure (50 lbs. per sq. in.). The analysis of the exit gases from the cracking operations under these conditions, using three different charging stocks, is given in Table 31. Acording to Wagner, the variation in the composition of these gases is illustrative of the corresponding changes in the liquid product. The increase in the per cent of methane and hydrogen (perhaps due to splitting of side chains from ring compounds) with increased carbon-hydrogen ratio in the feed stock is very marked. The corresponding decrease in the percentages of both ethylene and propene is also noteworthy.

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[40] M. S. Nemtzov, *loc. cit.*

[41] P. C. Keith, J. T. Ward and L. C. Rubin, *loc. cit.*

[42] A. W. Trusty, *loc. cit.*

[43] H. Sydnor, *Ind. Eng. Chem.*, 1934, **26**, 184; *Chem. Abs.*, 1934, **28**, 1849; *Brit. Chem. Abs.* B, 1934, 438; *J. Inst. Pet. Tech.*, 1934, **20**, 158A.

[44] A. W. Trusty, *loc. cit.*

[45] Discussions of cracking under pressure have been given by: A. N. Sachanen, *Erdöl u. Teer*, 1934, **10**, 105; *J. Inst. Pet. Tech.*, 1934, **20**, 412A; *Brit. Chem. Abs.* B, 1935, 7; *Chem. Abs.*, 1934, **28**, 7499. M. S. Nemtzov, *J. Inst. Pet. Tech.*, 1935, **21**, 644; *Neft. Khoz.*, 1933, **25** (10), 41; *J. Inst. Pet. Tech.*, 1935, **21**, 375A; *Chem. Abs.*, 1934, **28**, 3567; 1935, **29**, 6410; *Brit. Chem. Abs.* B, 1934, 866; 1935, 836.

TABLE 31.—*Analysis of Exit Gas from Vapor Phase Treatment of Different Charging Stocks Under the Same Cracking Conditions.*

	Cabin Creek Gas Oil	Spindletop Topped Crude	Polymerized Olefins
$CH_4 + H_2$	35.0	38.8	48.4
C_2H_4	24.6	20.3	14.2
C_2H_6	11.9	13.2	12.3
C_3H_6	18.0	13.1	12.6
C_3H_8	2.5	5.7	2.8
C_4 fraction	4.7	6.4	7.4
C_5 fraction and heavier	3.1	2.5	2.3

Aleksandrov[47] found that the gasoline yield could be increased by cracking narrow petroleum cuts under different thermal conditions. Low-boiling fractions gave optimum results when treated at high temperatures with long heating periods. High-boiling fractions, however, produce best yields of motor fuels when cracked at low temperatures with short times of contact.

Trusty[48] has shown that the chemical composition of the charge is quite important in determining the operating conditions. Since the paraffin hydrocarbons crack more readily than any other group, paraffinic base oils should be the easiest to decompose. The paraffins between dodecane ($C_{12}H_{26}$) and cetane ($C_{16}H_{34}$) are the most stable of these hydrocarbons. However, the stability decreases with the paraffins of higher molecular weight. The resultants of the cracking of paraffins are smaller paraffins and olefins. Naphthenes are more heat resistant than the paraffins and are dehydrogenated to aromatics during cracking. Cyclic hydrocarbons may occur in the feed stock or may be formed in the course of the reactions by polymerization of olefins resulting in the decomposition of the paraffins. Aromatics, however, require heating to a high temperature before undergoing rupture. The differences in the ease of cracking straight run gas oil and cracked gas oil are very marked and may be attributed directly to the difference in the chemical nature of these two substances. The former oil is of a paraffinic nature and tends to undergo decomposition quite readily. The latter oil, which is recovered from the reaction mixture of the straight run gas oil, is much more on the aromatic side and is considerably harder to crack.

Effect of Conversion Per Pass. The extent to which the cracking reactions are allowed to proceed before the tarry bodies and gasoline fractions are separated from the recycle oil is known as the conversion per pass. Sydnor[49] defines this quantity as the product of the percentage gasoline and the percentage fresh feed. Most cracking systems involve recycling or the return of a portion or all of the heavier residual oil produced to the feed stock, generally straight-run distillates. In these systems, the total feed rate (straight-run plus cycle oils) is maintained constant, and the quantity of straight-run gas oil added per unit of time must be the equivalent of the total material removed from the system in the form of gasoline, fuel oil, cycle gas oil, gas and coke. Keith and Montgomery[50] have stated that increasing the conversion per pass results in (1) a lower total yield of gasoline, (2) gasoline of a higher octane number, (3) a greater gas production and (4) an increased tendency toward coke formation.

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[46] C. R. Wagner, *Ind. Eng. Chem.*, 1934, 26, 188; *Chem. Abs.*, 1934, 28, 1849; *Brit. Chem. Abs.* B, 1934, 438; *J. Inst. Pet. Tech.*, 1934, 20, 178A. See also A. F. Dobryanskii, E. K. Kanep and S. V. Katzman (*Materials on Cracking and Chem. Treatment of Products Obtained*, *Khimteoret* (*Leningrad*), 1935, 2, 60; *Chem. Abs.*, 1935, 29, 5639; *Brit. Chem. Abs.* B, 1936, 483) who show that the yield of aromatic products obtained in vapor-phase cracking of various stocks is due directly to the amount of tar produced in the cracking operation.

[47] L. A. Aleksandrov, *Neft. Khoz.*, 1934, 26 (9), 57; *Chem. Abs.*, 1935, 29, 4557.

[48] A. W. Trusty, *Nat. Pet. News*, 1935, 27 (45), 34; *Chem. Abs.*, 1936, 30, 2734.

This factor is important because, if the cracking is carried out too far, the heavy residues will form coke. However, by removing the products from the zone of reaction and separating the objectionable materials, undesirable residues can be avoided to a large extent. In fact, only a limited amount of gasoline can be formed in each cracking stage.[51] The actual degree of cracking is, therefore, dependent upon the type of charging stock.[52] Thus, with a paraffinic base oil, a conversion per pass as high as 20 to 25 per cent can be used without excessive coke formation. On the other hand, with asphaltic base stocks this value should not exceed 10 to 15 per cent.[53] Dobryanskii, Kanep and Katzman have stated that too high a conversion per pass tends to "burning" the paraffinic constituents and condensing them to the more stable cyclic compounds.[54]

The diminution in the gasoline yield with increasing conversion is attributed primarily to the decomposition of the product already formed. According to Sachanen[55] the decomposition of the gasoline is negligible with conversions up to 20 per cent. However, for a 50 per cent possible yield per cycle the actual quantity of gasoline obtained is only about 41 per cent, the remaining 9 per cent being cracked to still lower molecular weight hydrocarbons.

Significance of Coke Formation in Cracking. The reactions involved in the cracking of an oil are of a progressive type. The resultants (e.g., gas, gasoline, intermediate oil, tar, coke and residue) do not form simultaneously during the breaking up of the original hydrocarbons. Especially in the case of coke formation, decomposition appears to proceed through the stages of intermediate oil, tar and finally coke.

However, as shown previously, coke will not be formed unless the conversion per pass is carried out beyond a definite point. This limit is determined by the composition of the compounds in the charging stock. Due to the fact that asphaltic base oils naturally contain tars, coke formation sets in more rapidly in this case than when cracking a paraffin base or a distilled oil.[56] Coke does not result from the primary decomposition of paraffins. On the other hand, a high temperature is required to crack the aromatics, and all of the coke formation is said to be traceable directly to this class of hydrocarbons. Hence the more aromatic the stock is initially the greater will be the proportion of coke. However, as was shown by Trusty in the case of cracked gas oil, coke can be obtained from an aromatic-free stock by prolonged heating which changes the nature of the stock to an aromatic type. Gerr[57] has suggested eliminating coke formation in high temperature vapor-phase cracking by vaporizing the oils and separating the vapors

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[49] H. Sydnor, *Ind. Eng. Chem.*, 1934, **26**, 184; *Chem. Abs.*, 1934, **28**, 1849; *Brit. Chem. Abs.* **B**, 1934, 438; *J. Inst. Pet. Tech.*, 1934, **20**, 158A.

[50] P. C. Keith and W. B. Montgomery, *Ind. Eng. Chem.*, 1934, **26**, 190; *Chem. Abs.*, 1934, **28**, 1848; *Brit. Chem. Abs.* **B**, 1934, 438; *J. Inst. Pet. Tech.*, 1934, **20**, 179A.

[51] S. N. Obryadchikov and M. M. Karasik (*Neft*, 1936, **7** (6), 17; *Chem. Abs.*, 1936, **30**, 6175; *J. Inst. Pet. Tech.*, 1936, **22**, 448A) have shown that the conversion per pass may be increased by about 3 per cent in vapor-phase treatment by the introduction of a reaction chamber.

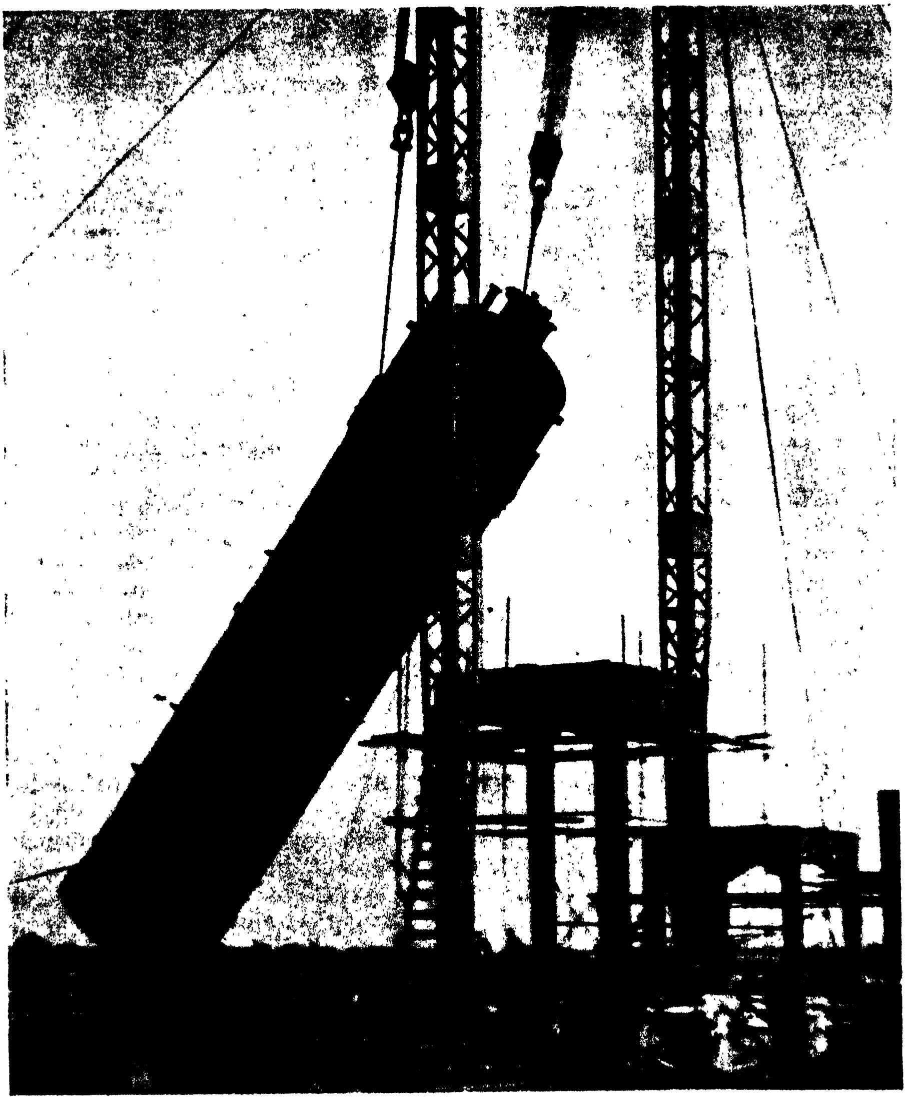
[52] The relationship of conversion per pass to allowable boiling range of charging stock for various cracking processes is discussed by P. C. Keith and W. B. Montgomery, *loc. cit.*

[53] A. W. Trusty, *loc. cit.*

[54] A. F. Dobryanskii, E. K. Kanep and S. V. Katzman, *Materials on Cracking and Chem. Treatment of Products Obtained, Khimteoret* (*Leningrad*), 1935, **2**, 60; *Chem. Abs.*, 1935, **29**, 5639; *Brit. Chem. Abs.* **B**, 1936, 483.

[55] A. N. Sachanen, *Erdöl u. Teer*, 1934, **10**, 105; *J. Inst. Pet. Tech.*, 1934, **20**, 412A; *Brit. Chem. Abs.* **B**, 1935, 7; *Chem. Abs.*, 1934, **28**, 7499.

[56] A. W. Trusty, *loc. cit.* See also A. N. Sachanen, *loc. cit.*



Courtesy Standard Oil Co. of California

FIG. 27A.—Welded Steel Pressure Vessel Being Raised into Position.

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[57] V. F. Gerr, *Trans. 1st All Union Sci.-Eng.-Tech. Soc. Petroleum Workers, Baku, 1933, Gosud. Nauch. Tekh. Gorno-Geol., Neft. Izdat.*, 1934 (3), 137; *Chem. Abs.*, 1935, 29, 4557.

from the residue in a step previous to the cracking. Light preliminary cracking in order to break down the heavy oil fractions has also been proposed to prevent excessive carbonization.[58]

Butkov and Ostrovai[59] reported that coke exerts a strong catalytic action on the secondary reactions in high temperature cracking. Condensation reactions, according to the views of these investigators, are heterogeneous and are catalyzed by the coke formed in the retort. Consequently a small amount of coke in the apparatus promotes higher yields of aromatic compounds. On the other hand larger quantities effect more pronounced condensation, which is accompanied by lower yields of aromatic compounds, gas and light oils. Heavy cracking carried out in a retort free of coke results in a low yield of aromatics and a high yield of gas. Butkov and Ostrovai have stated that the amount of coke produced in commercial cracking operations depends upon the stock and in general varies from 1.2 to 9 per cent.

CATALYSTS

A large number of substances have been suggested as promoters for the cracking of petroleum fractions.[60] Borisov and Gaverdovskaya[61] investigated the vapor-phase catalytic cracking of gas oil, kerosene and various hydrocarbons found in petroleum (such as hexane, cyclohexane, methylcyclohexane and dimethylcyclohexane). In these tests, zinc oxide, nickel oxide (Ni_2O_3), alumina, uranyl oxide (UO_3), titanium dioxide, thorium dioxide, nickel wire and nickel precipitated on alumina, activated carbon, activated bone charcoal, glass chips and fused borax were used. The best yield of gasoline from gas oil was obtained by cracking at 550°C. in the presence of nickel oxide and amounted to 38.0 per cent. Under the same temperature conditions without an activator, the conversion was only 18.2 per cent. In the case of kerosene, the effect of catalysts is even more pronounced. Pure thermal treatment at 500°C. gave a gasoline yield of 7.8 per cent. With uranyl oxide, the gasoline yield was increased to 26.4 per cent, and with activated carbon, 33.8 per cent. In the presence of uranyl oxide, branched cycloparaffins underwent demethanation in addition to dehydrogenation.

The use of coke formed in the reaction chamber as a catalytic agent has already been discussed. The action of a wide variety of forms of activated carbon has also been investigated. Morrell[62] suggested mixing finely divided solid bituminous material, such as coal or lignite, with the oil. The low-boiling products obtained by cracking this mixture are said to be of high antiknock value. Fields[63] has mentioned the addition of a small percentage of finely divided vegetable material, such as sawdust or beet pulp, to the oil. The suspension is heated to 750°C. to effect simultaneous cracking of the oil and carbonization of the solid material. Cotton wool may also be employed at temperatures of 300-350°C., according to Oppenheim.[64] Zurcher[65] proposes to utilize petroleum coke, activated by treatment with steam and phosphoric acid. Activated carbon, impregnated with a solution of potassium silicate, potassium carbonate, potassium chloride and potassium sulphate, or sodium carbonate and sodium chloride, and calcined has been found to be an activator for the cracking of mineral oils.[66] Zinc chloride may also be substituted as an impregnating agent.[67] Pier and Donath[68] prepare a catalyst by mixing ammonium vanadate, cobalt nitrate and phosphoric acid with activated charcoal and heating the resulting magma for about 6 hours in the presence of hydrogen and carbon disulphide at 350°C. This catalyst is recommended for reforming gasoline at temperatures of 430-450°C. Towne[69] has suggested the use of silica gel in which activated carbon is imbedded as a catalyst in treatments to increase the antiknock value of gasolines. In this case, however, the process is carried out at 500-700°C.

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[58] Y. Blyakher, S. N. Obryadchikov, E. Smidovich and S. Khaiman, *Neft. Khoz.*, 1934, **26** (9), 51; *Chem. Abs.*, 1935, **29**, 4557; *Brit. Chem. Abs.* **B**, 1936, 227.

[59] N. A. Butkov and E. Y. Ostrovai, *Neft. Khoz.*, 1935, **27** (2), 75; *Chem. Abs.*, 1935, **29**, 4926; *Brit. Chem. Abs.* **B**, 1936, 402.

[60] In this connection see the so-called Houdry Process, which is discussed on the following pages.

[61] P. P. Borisov and M. V. Gaverdovskaya, *Neft. Khoz.*, 1934, **26** (10), 37; *Chem. Abs.*, 1935, **29**, 4558; *Brit. Chem. Abs.* **B**, 1936, 227.

[62] J. C. Morrell, U. S. P. 1,972,944, Sept. 11, 1934, to Universal Oil Products Co.; *Chem. Abs.*, 1934, **28**, 6985; *J. Inst. Pet. Tech.*, 1934, **20**, 579A. British P. 409,969, 1934; *Brit. Chem. Abs.* **B**, 1934, 708.

[63] I. D. Fields, U. S. P. 1,959,467, May 22, 1934; *Chem. Abs.*, 1934, **28**, 4589; *Brit. Chem. Abs.* **B**, 1935, 260.

[64] R. Oppenheim, U. S. P. 1,960,951, May 29, 1934, to Soc. anon. le Carbone; *Chem. Abs.*, 1934, **28**, 4590; *J. Inst. Pet. Tech.*, 1934, **20**, 465A.

[65] P. Zurcher, U. S. P. 1,895,063, Jan. 24, 1933, to Continental Oil Co.; *Brit. Chem. Abs.* **B**, 1933, 902; *Chem. Abs.*, 1933, **27**, 2572.

Lelgemann[70] has studied the catalytic action of nitrosyl chloride (NOCl) in conjunction with aluminum, iron, aluminum chloride, iron chloride and calcium oxide in cracking various petroleum fractions. In this treatment, the metallic promoter is added to the cracking stock and a small amount of nitrosyl chloride (about 0.1 per cent) is introduced continuously into the reaction chamber. Thus, by interaction with the nitrosyl chloride the activity of the metallic promoter is constantly regenerated. The proportions of solid catalyst are given as: with calcium oxide, 5 per cent; with powdered aluminum, about 0.08 per cent; with aluminum chloride, 7.4 per cent and with aluminum chloride and ferric chloride together, 12 per cent. Gifford[71] has cracked oils at temperatures as low as 150-300°C. by using a catalyst composed of aluminum chloride, zinc chloride or magnesium chloride, mixed with bauxite. Marconi[72] has suggested the addition of oxidizing agents (manganese dioxide, lead chromate or copper oxide) to the combinations of various metallic halides, for instance boron trifluoride and aluminum chloride or antimony and aluminum chlorides, as a catalyst for cracking reactions. In a method introduced by Dubbs[73] streams of oil and an inert gas (e.g., carbon dioxide or flue gas) and aluminum chloride or nickel oxide are separately preheated, mixed and passed into a heated reactor. The pressure is increased in the latter step and thermolization is effected with the promoter suspended in the oil. Stratford[74] advocates employment of clay which has been utilized previously in the refining of lubricating oils.

Trumble and Seeley[75] propose to effect decomposition by means of a catalytic mixture of molten lead and nickel oxide. On the other hand, Cristescu and Stavrat[76] prefer alloys of two or more metals, for example, antimony, silver, chromium, tin and zinc, such that the specific heat of the metallic mix is less than 0.1. Alloys of lead and sodium (90 and 10 per cent respectively) are also said to be effective in their action.[77] Towne[78] recommends the use of molten selenium at 400-600°C. under pressures of about 300 lbs. per sq. in. in reforming gasoline. Tubes constructed of palladium-molybdenum-chromium-nickel alloys have been employed by Ocun[79] to promote decomposition. In this process, the stock is preheated to below the cracking temperature and vaporized under pressure in the presence of hydrogen. The vapors are then subjected to the action of superheated steam and rapid cracking at 1000-1500°F. and immediately allowed to expand and cool. Cracking may be brought about by heating heavy hydrocarbons to 350-550°C. under pres-

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[66] H. Herbst, *Chem.-Ztg.*, 1934, **58**, 881: *Brit. Chem. Abs.* **B**, 1934, 1091; *J. Inst. Pet. Tech.*, 1935, **21**, 18A; *Chem. Abs.*, 1935, **29**, 2701.

[67] British P. 411,477, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 6993; *Brit. Chem. Abs.* **B**, 1934, 789.

[68] M. Pier and E. Donath, U. S. P. 1,975,476, Oct. 2, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 7517.

[69] C. C. Towne, U. S. P. 1,967,636, July 24, 1934, to Texas Co.; *Chem. Abs.*, 1934, **28**, 5976; *J. Inst. Pet. Tech.*, 1934, **20**, 533A.

[70] W. Lelgemann, U. S. P. 1,971,190, Aug. 21, 1934, to Hydrocarbon Processes Inc.; *Chem. Abs.*, 1934, **28**, 6558; *Brit. Chem. Abs.* **B**, 1935, 793; *J. Inst. Pet. Tech.*, 1934, **20**, 578A. U. S. P. 2,015,529, Sept. 24, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 420A; *Chem. Abs.*, 1935, **29**, 8316; *Brit. Chem. Abs.* **B**, 1936, 1079. Canadian P. 348,960, 1935; *Chem. Abs.*, 1935, **29**, 3820. British P. 430,748, 430,813-4, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 343A. French P. 779,578, 1935; *Chem. Abs.*, 1935, **29**, 5647.

[71] H. W. F. Gifford, British P. 445,757, 1936; *Brit. Chem. Abs.* **B**, 1936, 680; *Chem. Abs.*, 1936, **30**, 6935; *J. Inst. Pet. Tech.*, 1936, **22**, 312A.

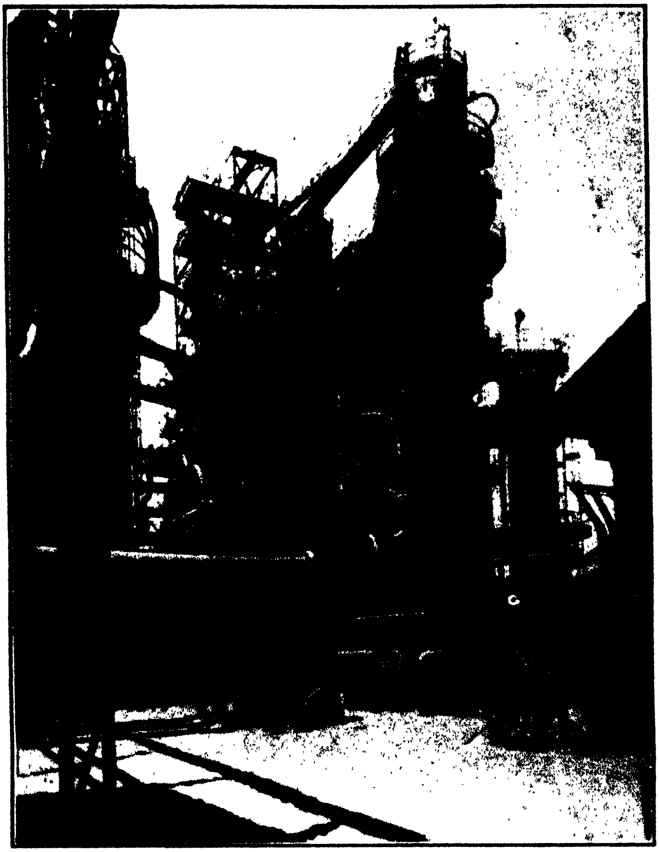
[72] M. A. Marconi, British P. 410,741, 1934; *J. Inst. Pet. Tech.*, 1934, **20**, 463A; *Brit. Chem. Abs.* **B**, 1934, 791; *Chem. Abs.*, 1934, **28**, 6294.

[73] L. A. Dubbs, U. S. P. 2,051,471, Aug. 18, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 449A; *Chem. Abs.*, 1936, **30**, 6935.

[74] R. K. Stratford, British P. 456,244, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1937, **31**, 2408.

[75] M. J. Trumble and W. L. Seeley, U. S. P. 1,938,877, Dec. 12, 1933, to Petroleum Hydrogenation Co., Ltd.; *Chem. Abs.*, 1934, **28**, 1519; *J. Inst. Pet. Tech.*, 1934, **20**, 108A.

[76] J. Cristescu and G. Stavrat, French P. 774,231, 1934; *Chem. Abs.*, 1935, **29**, 2343.



Courtesy Universal Oil Products Co.

FIG. 28.—Dubbs Multiple Coil Cracking Unit.

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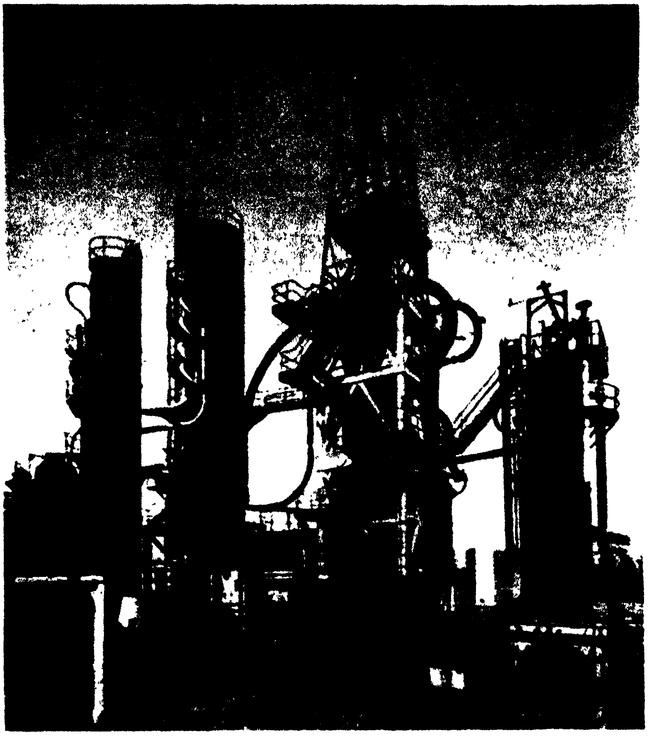
[77] O. E. Roberts, Jr., U. S. P. 2,027,552, Jan. 14, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 157A; *Chem. Abs.*, 1936, **30**, 1549; *Brit. Chem. Abs.* B, 1937, 113. See also J. F. Wait, U. S. P. 2,052,812, Sept. 9, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 543A; *Chem. Abs.*, 1936, **30**, 7322 who proposes to crack hydrocarbons in the presence of an alkali metal to promote molecular rearrangement and association of the vapors.

[78] C. C. Towne, U. S. P. 1,997,159, Apr. 9, 1935, to Texas Co.; *Chem. Abs.*, 1935, **29**, 3821; *J. Inst. Pet. Tech.*, 1935, **21**, 217A.

[79] E. A. Ocun, U. S. P. 2,052,148, Aug. 25, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 449A; *Chem. Abs.*, 1936, **30**, 6935.

sure of 90 to 100 atmospheres in the presence of finely granulated metals and acids or chlorinated hydrocarbons capable of forming acids under the operating conditions.[80] Among the metals suggested are: vanadium, chromium, molybdenum, tungsten, manganese, nickel, iron, aluminum and zinc. Hydrochloric, sulphuric, nitric, phosphoric, and sulphonic acids, or acid salts are recommended for use in conjunction with the above metals, however, chloroform, bromoform, carbon tetrachloride and dichloroethane may also be employed. Moehrle[81] found that by heating hydrocarbons with about 1 per cent of iodine at 350° to 550°C. under 50 atmospheres pressure, cracking and polymerization of the olefins formed by the primary reactions could be brought about. A system involving progressive catalysis has been investigated.[82] In this method, the hydrocarbon vapors are mixed with steam and passed first over activated fuller's earth at 300-350°C., then over pumice stone impregnated with nickel, cobalt or copper at 300-450°C. and finally over activated fuller's earth mixed with nickel oxide, cobalt oxide or alumina at 150°



Courtesy Industrial and Engineering Chemistry

FIG. 29.—Dubbs Combination Topping and Cracking Unit. (G. Egloff and J. C. Morrell)

to 300°C. Winkler and Haeuber[83] prefer to dilute the hydrocarbon vapors with nitrogen and to conduct the cracking at about 700°C. in the presence of elementary silicon. The use of activated aluminum hydrosilicate has also been investigated.[84]

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[80] British P. 442,371, 1936 and 442,592, 1936, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1936, 438; *J. Inst. Pet. Tech.*, 1936, **22**, 209A. British P. 451,656, 1936; *Brit. Chem. Abs.* **B**, 1936, 969. French P. 790,829, 1935, 791,070, 1935, and 795,785, 1936; *Chem. Abs.*, 1936, **30**, 3217, 3218, 5777.

[81] E. Moehrle, U. S. P. 1,954,573, Apr. 10, 1934; *Brit. Chem. Abs.* **B**, 1935, 135; *Chem. Abs.*, 1934, **28**, 3885; *J. Inst. Pet. Tech.*, 1934, **20**, 423A.

[82] German P. 585,609, 1933, to Gewerkschaft Kohlenbenzin; *Chem. Abs.*, 1934, **28**, 1518.

Ellis[85] recommends the use of catalysts such as molybdenum or tungsten oxides for cracking heavy petroleum oils containing sulphur compounds and simultaneously hydrogenating and methanating the products. In this procedure, the oil together with a gas mixture composed of hydrogen, methane and small amounts of carbon monoxide is heated to 480-550°C. under a pressure of about 50 atmospheres in the presence of the catalyst. The amount of hydrogen introduced should be insufficient to form a saturated liquid product under the reaction conditions. The liquid obtained from this treatment has been shown to have most of the original sulphur content removed as hydrogen sulphide. Egloff,[86] on the other hand, suggests the cracking of oils in the presence of finely divided alkali or alkaline earth hydrides (such as sodium hydride, NaH, or calcium hydride, CaH_2). This method is reported to hydrogenate the highly unsaturated hydrocarbons which are formed in cracking and to desulphurize the product. Hypochlorous acid vapor may also be used in vapor-phase processes to reduce the sulphur content of liquid products.[87]

The antiknock qualities of motor fuels are said to be improved by passing the gasoline vapors over phosphate catalysts at temperatures below the cracking range.[88] Granular boron phosphate (BPO_4), prepared by heating orthoboric acid with phosphoric acid on a steam bath has been suggested for this purpose. By passage over the contact agent at 450°C., the octane number of a straight run gasoline was reported to have been bettered from its initial value 55 to 62.5 without substantial loss due to the formation of gases.

COMMERCIAL CRACKING PROCESSES

The commercial processes employed in cracking may be divided into two general types, vapor and vapor-liquid phase operations. In the first type, the cracking reactions generally take place in the range of 500-600°C. (850-1150°F.) and at atmospheric or slightly super-atmospheric pressure, so that the hydrocarbons are in the vapor state. In the vapor-liquid or mixed phase type, treatment is carried out at lower temperatures, ordinarily 390-500°C. (750-850°F.), and under pressures of 200 to 1500 lbs. per sq. in. Formerly the latter type of processes was known as "liquid phase," but Sydnor[89] has stated that under the conditions employed, some of the hydrocarbons were undoubtedly vaporized so that a mixed phase system results. According to Sydnor, however, there are three reasons for maintaining the pressure operations: (1) the reduction of gas and coke formation, (2) better quality of distillate as regards ease of finishing and (3) higher capacity of apparatus secured in this case.

Developments in the design and operation of the various types of cracking plants have been influenced by a number of factors in addition to the increased

[83] F. Winkler and H. Haeuber, U. S. P. 1,973,834, Sept. 18, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 6994.

[84] J. P. Daugherty, Jr., U. S. P. 2,031,591, Feb. 25, 1936, to Houdry Process Corp.; *Chem. Abs.*, 1936, **30**, 2361; *J. Inst. Pet. Tech.*, 1936, **22**, 149A. See also the Houdry Process.

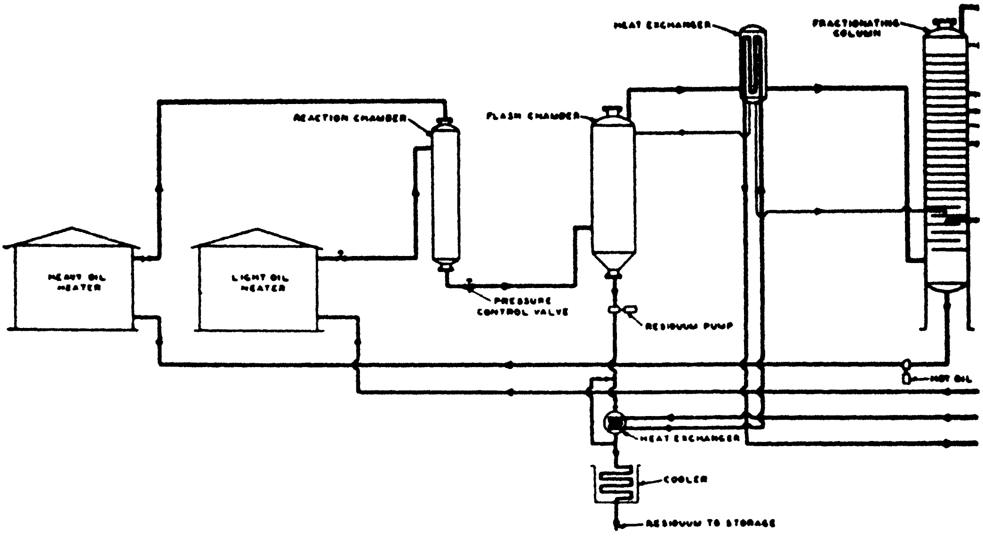
[85] Carleton Ellis, U. S. P. 1,966,790, July 17, 1934, to Standard-I. G. Co.; *Chem. Abs.*, 1934, **28**, 5652; *Brit. Chem. Abs.* **B**, 1935, 441.

[86] G. Egloff, U. S. P. 1,950,721, Mar. 13, 1934, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1935, 215; *Chem. Abs.*, 1934, **28**, 3577.

[87] G. Egloff, U. S. P. 1,986,190, Jan. 1, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 1239; *Brit. Chem. Abs.* **B**, 1936, 357.

[88] British P. 446,621, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 6938; *Brit. Chem. Abs.* **B**, 1936, 584. See also F. R. Moser, Canadian P. 362,665, 1936, to Shell Development Co.; *Chem. Abs.*, 1937, **31**, 1603.

[89] H. Sydnor, *Ind. Eng. Chem.*, 1934, **26**, 184; *Chem. Abs.*, 1934, **28**, 1849; *Brit. Chem. Abs.* **B**, 1934, 438; *J. Inst. Pet. Tech.*, 1934, **20**, 158A.



demand for high-octane gasoline. The aim of many of the improvements has been to increase the flexibility of operation, gasoline yields, length of runs, quality of tar (by reduction in coke formation) and to effect economies in fuel consumption. Developments of major importance include the use of multiple coil and combination units, the primary cracking of heavy residues to facilitate subsequent cracking and the reforming of gasolines[90] for the production of higher octane motor fuels.[91]

In multiple coil cracking, the charging stock is separated into two or more fractions each of which is cracked in separate units under conditions most favorable for efficient operation. In certain plants, distillation of crude oil, viscosity breaking (primary cracking), naphtha reforming and multiple coil cracking can all be carried out in one unit. Primary cracking consists in subjecting the heavy oil under treatment to an initial conversion per pass of 8 to 10 per cent. This operation results in the production of some gasoline as well as a large proportion of oil of a lower boiling point and lower molecular weight than the feed stock. The latter fraction may be cracked under relatively severe conditions, that is, at a high conversion per pass.

A complete discussion of cracking plants is beyond the scope of this volume. Only the principles and general procedure involved in the various processes will be briefly considered.[92]

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[90] For a discussion of reforming, consult G. Egloff, E. F. Nelson and G. B. Zimmerman, *Oil & Gas J.*, 1935, 34 (32), 90; *Chem. Abs.*, 1936, 30, 2735.

[91] Developments in the oil cracking art are described by: P. C. Keith and W. B. Montgomery, *Ind. Eng. Chem.*, 1934, 26, 190; *Chem. Abs.*, 1934, 28, 1848; *Brit. Chem. Abs.* B, 1934, 438; *J. Inst. Pet. Tech.*, 1934, 20, 179A. G. Egloff and E. F. Nelson, *Oil & Gas J.*, 1936, 35 (6), 50; (7), 34; (8), 43; *Chem. Abs.*, 1936, 30, 7828; *J. Inst. Pet. Tech.*, 1936, 22, 446A, 447A, 504A. *Chem. Eng. Cong. World Power Conf.*, 1936, C13, 1; *Brit. Chem. Abs.* B, 1936, 774. A. Feigin and V. A. Butkov, *Neft. Khoz.*, 1933, 25 (10) 45; 1934, 26 (1), 40; *Chem. Abs.*, 1934, 28, 3571; *J. Inst. Pet. Tech.*, 1934, 20, 496A. E. Stoicovici, *Mon. pétrole roumain.*, 1936, 37, 587; *Chem. Abs.*, 1936, 30, 7828.

[92] For a discussion of the earlier commercial cracking processes, see Carleton Ellis, "The Chem-

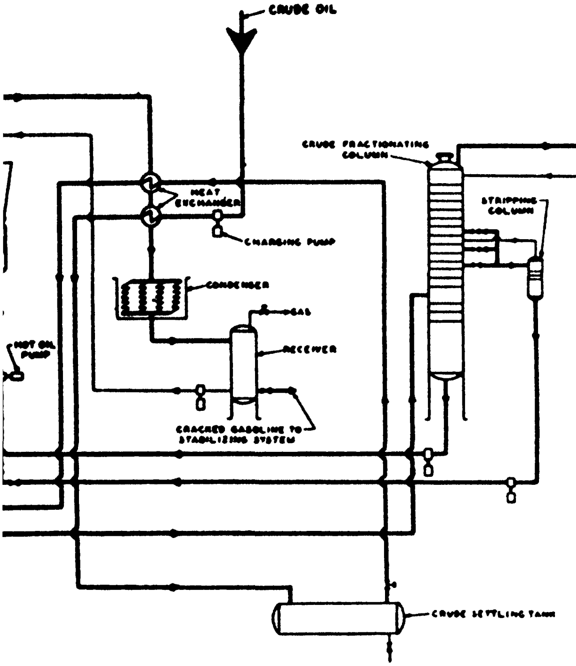


FIG. 30.
Flow Sheet of Dubbs Multiple Coil Unit. (G. Egloff and E. F. Nelson)

Courtesy Universal Oil Products Co.

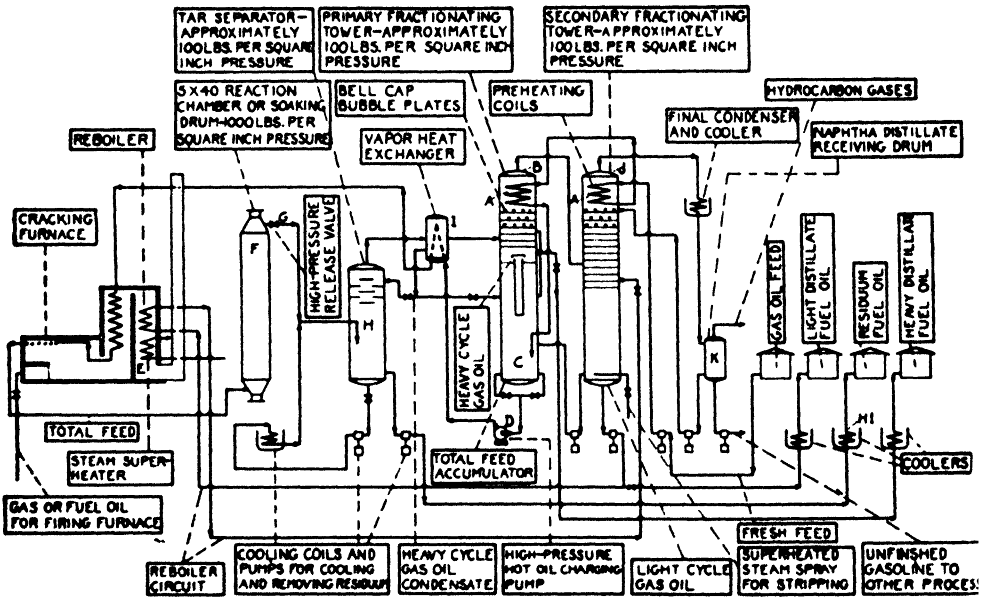
Dubbs Process. A flow sheet of the Dubbs multiple coil unit,[93] one of the vapor-liquid phase type, is shown in Fig. 30. The crude oil as charged usually contains water as an emulsion which is separated from the oil in a settling tank. The crude oil is then passed to the crude fractionating column (about 7 feet in diameter and 47 feet high) from which straight-run gasoline, light oil (naphtha and kerosene) and heavy oil (topped crude) are obtained. The topped crude is pumped directly to a second column and is contacted with hot vapors from the cracking unit, causing a partial fractionation. The vapors from this column (10 feet in diameter and 58 feet high) are split into a liquid side cut which is pumped to a light oil heater and heated to 975°F. under 600 lbs. per sq. in. pressure and into an overhead consisting of vaporized gasoline and gas. The bottoms from this column are fed to a heavy oil preheater and heated to 910°F. at 300 lbs. per sq. in. pressure. Both heaters discharge to a reaction chamber under 300 lbs. per sq. in. pressure from which the material is fed into a flash chamber, where the pressure is reduced to about 75 lbs. per sq. in. The vapors from the top of the flash chamber are cooled and returned to the second fractionating column.

Tube and Tank Process. In the Tube and Tank process (also of the mixed phase type), the cracking reactions usually are carried out under high pressure (750-1000 lbs. per sq. in.). A flow sheet of a typical unit using this type of operation is given in Fig. 31. The fresh charging stock (normally gas oil) is preheated and introduced into a primary fractionating column, where it is contacted with cracked gasoline and cycle stock vapors. The cycle stock is condensed and

istry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. Also, A. N. Sachanen and M. D. Tilicheyev, "Chemistry and Technology of Cracking," The Chemical Catalog Co., Inc., New York, 1932.

[93] G. Egloff and E. F. Nelson, *loc. cit.* See also G. N. Critchley, *Fuel*, 1934, **13**, 100; *Brit. Chem. Abs.* **B**, 1934, 486; *J. Inst. Pet. Tech.*, 1934, **20**, 363A; *Chem. Abs.*, 1934, **28**, 6987; *Petroleum Times*, 1935, **34**, 521; *J. Inst. Pet. Tech.*, 1936, **22**, 49A.

returned to the accumulator from which the fresh and cycle oil mixture (total feed) is pumped under pressure through the tubes of the heating furnace (maintained at 850° to 900°F.) and then into the reaction chamber where the bulk of the cracking takes place under a pressure of about 1000 lbs. per sq. in. The oil next flows to a separator, where the fuel oil portions are removed. The vapors from the separator are fed into the primary fractionating column under 100 lbs. per sq. in. pressure, where a portion of the cycle gas oil is removed. The vapors from this feed are now passed into a secondary column. The overhead from this treatment is conducted into a disengaging drum and the gas is separated from the gasoline.[94]


TAR SEPARATOR—APPROXIMATELY 100LBS. PER SQUARE INCH PRESSURE
PRIMARY FRACTIONATING TOWER—APPROXIMATELY 100LBS. PER SQUARE INCH PRESSURE
SECONDARY FRACTIONATING TOWER—APPROXIMATELY 100LBS. PER SQUARE INCH PRESSURE
5X40 REACTION CHAMBER OR SOAKING DRUM—1000LBS. PER SQUARE INCH PRESSURE
BELL CAP BUBBLE PLATES
PREHEATING COILS
HYDROCARBON GASES
FINAL CONDENSER AND COOLER
NAPHTHA DISTILLATE RECEIVING DRUM
REBOILER
VAPOR HEAT EXCHANGER
CRACKING FURNACE
HIGH-PRESSURE RELEASE VALVE
HEAVY CYCLE GAS OIL
GAS OIL FEED
LIGHT DISTILLATE FUEL OIL
RESIDUUM FUEL OIL
HEAVY DISTILLATE FUEL OIL
A
B
C
D
E
F
G
H
I
K
H1
TOTAL FEED
STEAM SUPER-HEATER
TOTAL FEED ACCUMULATOR
COOLERS
GAS OR FUEL OIL FOR FIRING FURNACE
FRESH FEED
REBOILER CIRCUIT
COOLING COILS AND PUMPS FOR COOLING AND REMOVING RESIDUUM
HEAVY CYCLE GAS OIL CONDENSATE
HIGH-PRESSURE HOT OIL CHARGING PUMP
LIGHT CYCLE GAS OIL
SUPERHEATED STEAM SPRAY FOR STRIPPING
UNFINISHED GASOLINE TO OTHER PROCES

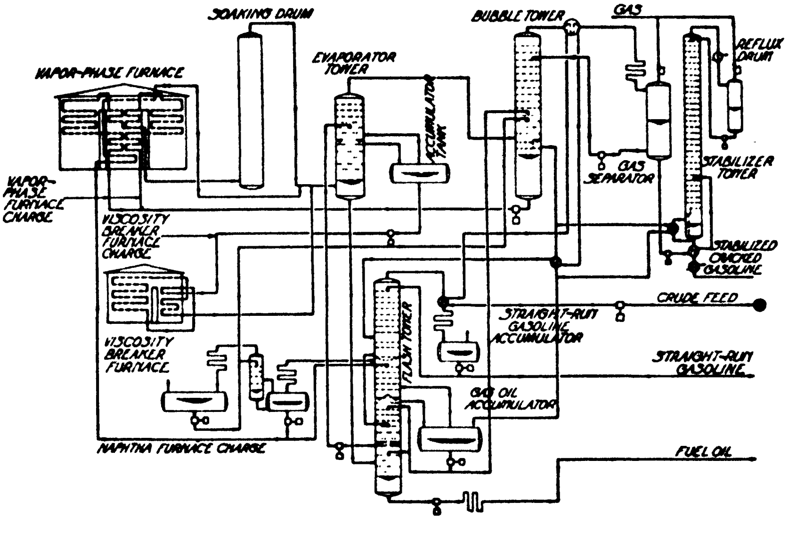
Courtesy Industrial and Engineering Chemistry

FIG. 31.—Flow Sheet of Tube and Tank Process. (H. Sydnor)

Cross Process. A flow sheet of the improved Cross process is shown in Fig. 32. In the earlier Cross method, the conversion per pass was too high to utilize residual oils as charging stocks. To overcome this limitation the manner of treatment was altered and primary cracking or viscosity breaking was employed. Further modifications have been introduced so that charging stocks varying from heavy fuel oil to the lightest kerosenes may be treated.[95] In the unit shown in Fig. 32 the straight-run gasoline is removed and reformed at 1000°F. and 750 lbs. per sq. in. The topped crude is split into two fractions, residuum oil and light gas oil. The former, together with the heavy recycle stock, are cracked in a primary chamber at 890°F. under a pressure of 250 lbs. per sq. in. The light gas oil, together with the light recycle stock, is cracked in the vapor phase at 940°F. and 200 lbs. per sq. in. pressure, using a furnace and reaction drum. The cracked gasoline is fractionated, condensed and separated from the waste gases while still under pressure.

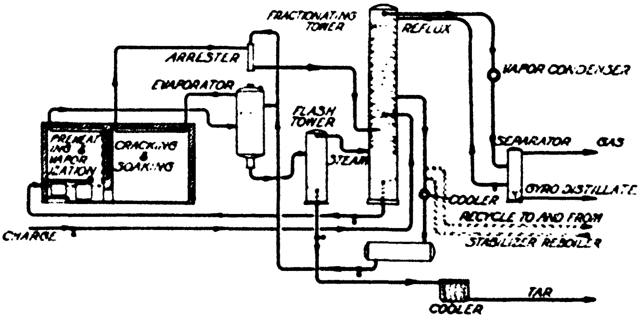
[94] H. Sydnor, *loc. cit.*
[95] P. C. Keith and W. B. Montgomery, *loc. cit.*

Gyro Process. The Gyro process is an important vapor-phase unit which has been developed along the lines of Hall's general procedure.[96] Keith and Montgomery[97] have stated that an inherent inability of this process to handle residue stocks has been overcome by the provision for the predistillation of heavy charging stocks. This is accomplished by passing a heavy stock combined with recycle oil through a pipe still into a vaporizer. The vapors are freed from entrained liquid



Courtesy Industrial and Engineering Chemistry

FIG. 32.—Flow Sheet of Cross Process. (P. C. Keith and W. B. Montgomery)



Courtesy Industrial and Engineering Chemistry

FIG. 33.—Flow Sheet of Gyro Process. (P. C. Keith and W. B. Montgomery)

and fed into the cracking chamber where the temperature is rapidly raised to 1100°F. Immediately after leaving the chamber, the vapors are contacted with cooled recycle gas oil. The temperature is thus reduced to 700°F., and the effects of polymerization and over-cracking are greatly reduced or eliminated. A flow sheet of this process is shown in Fig. 33. The entire process operates at atmospheric pressure.

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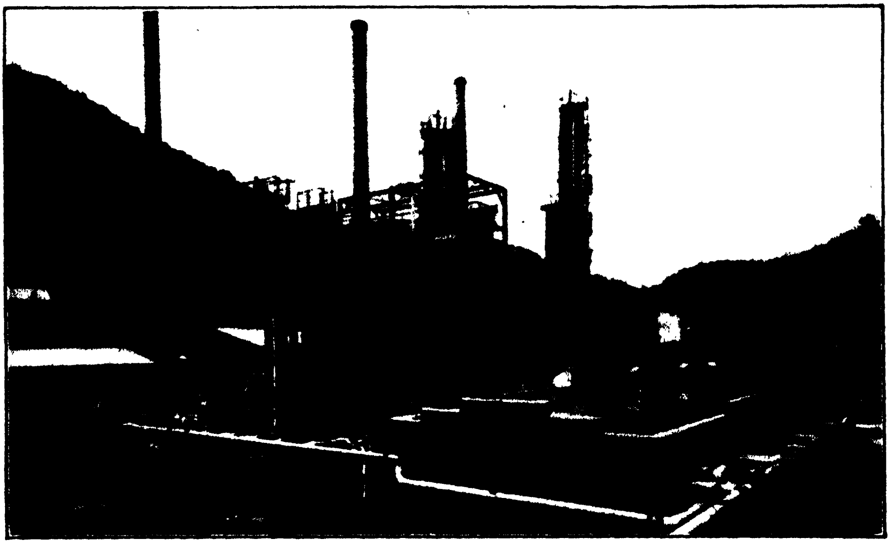
[96] The Hall process was introduced in 1914. See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934, 164, for a discussion of this method.

[97] P. C. Keith and W. B. Montgomery, *loc. cit.* See also G. N. Critchley, *loc. cit.* K. Kudo. *J. Fuel Soc. Japan*, 1936, 15, 709; *Chem. Abs.*, 1936, 30, 6929, has described a Gyro vapor phase unit incorporating a thermal polymerization unit. (See Chapter 26 for a discussion of the latter topic.)

De Florez Process. The de Florez type of operation is applicable for the handling of feed stocks varying from kerosene to heavy pitches.[98] Fig. 35 is a flow diagram for a typical installation for cracking reduced crude oil. After preheating and passage through a tar stripper,[99] the stock is fed into an evaporator and vaporized at about 790°F. and 165 lbs. per sq. in. pressure. The lower-boiling portions enter the bubble tower, and the heavier fractions are fed into a reaction chamber (maintained at about 880°F. and 330 lbs. per sq. in.), where they are mixed with recycle material (bottoms from the bubble tower) which has been cracked by heating at 630°F. and 900 lbs. per sq. in. to 1000°F. and 350 lbs. per sq. in. in a furnace. Vapors from the reaction chamber are returned into the evaporator and the high-boiling liquid portions are recycled to the tar stripper. Bottoms from the stabilizer and absorber units are recirculated to the evaporator and bubble tower.



Courtesy Alco Products, Inc.

FIG. 34.—Gyro Process Cracking Equipment.

A de Florez cracking unit incorporating coking operation is represented in Fig. 36. In this case, the feed (reduced crude oil) enters the evaporator under 100 lbs. per sq. in. pressure. The lower-boiling portion (below 680°F.) is introduced into the bubble tower. The bottoms from the distillation column are heated in a furnace to 1010°F. under 300 lbs. per sq. in., mixed with the high-boiling residue from the evaporator and passed into a coking drum. Here at 880°F. and 250 lbs. per sq. in. with long periods of contact, the heavy residua are reduced to coke and vapors, the latter being returned to the evaporator. The coking drums are ordinarily about 40 feet high, and can be filled to a height of 30 or 35 feet with coke. Using two drums, to permit continuous operations, runs of as long as 3000 hours

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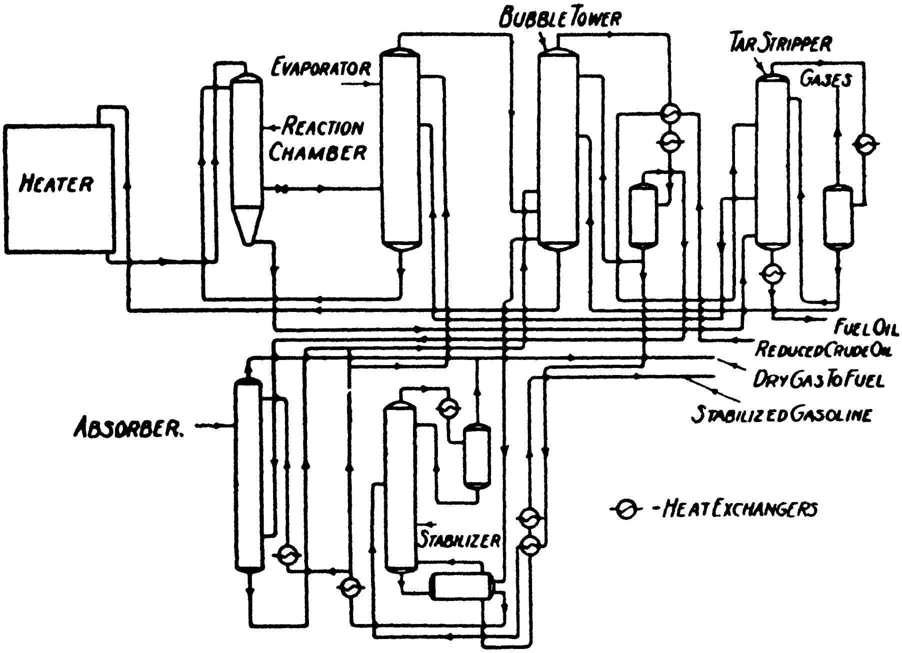
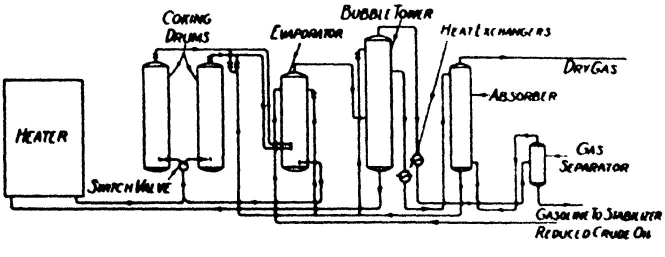
[98] Discussions of the de Florez process have been given by J. H. Hirsch (*World Petroleum*, 1932, 3 (3), 335; *Chem. Abs.*, 1932, 26, 6109), and P. C. Keith and W. B. Montgomery (*loc. cit.*).

[99] The function of the tar stripper is to separate the light heads and heavy bottoms from the stock. The former are introduced directly into the bubble tower, as reflux, and the latter are removed as fuel oil.



Courtesy Dr. Luis de Florez

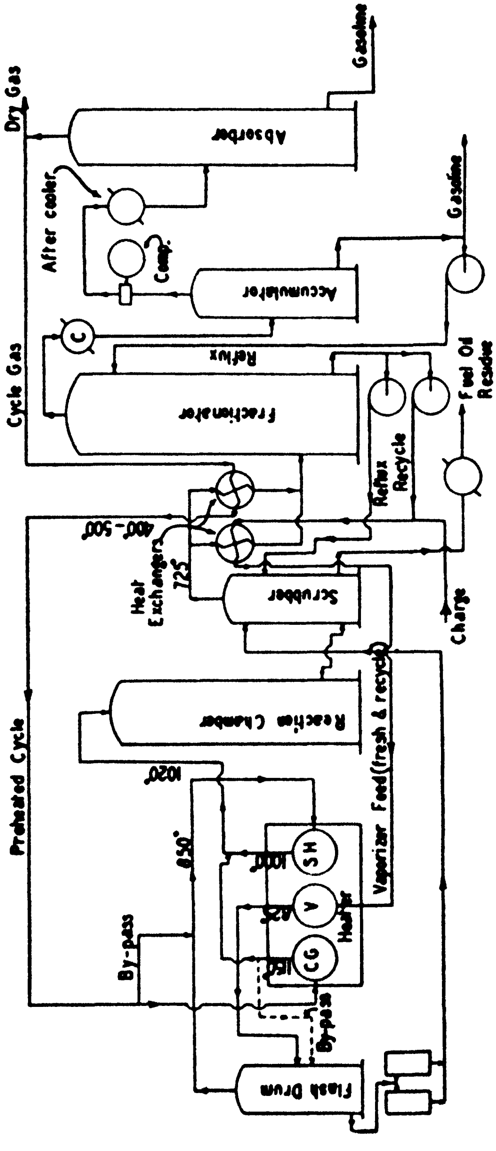
FIG. 35.—Flow Sheet of de Florez Method for Cracking Reduced Crude Oil.



Courtesy Dr. Luis de Florez

FIG. 36.—Flow Diagram of de Florez Cracking Unit with Coking Operation.

duration have been reported.[100] The coke, amounting to about 21 per cent of the total product, contains from 7 to 8 per cent of volatile matter and is low in ash.



Courtesy Oil and Gas Journal

Fig. 37.—Flow Sheet of True Vapor Phase Process.

T.V.P. Process. A description of the improved T.V.P. (True Vapor Phase) process has been given by Williams.[101] An important development in this method has been the replacement by tubular heaters of the "stoves" of the blast furnace type which were used formerly. The charge, ranging from heavy naphthas to heavy reduced crudes, is preheated by means of scrubber vapors, passed into a vaporizer (heated to 800-825°F.) and then into a flash drum, where vaporization is effected by means of hot gas. The vapors are then fed into a superheater coil where the temperature is raised to 1000°F. and finally enter the reaction chamber. Cycle gases (heated to 1150°F.) are introduced into the flash drum, superheater or reaction chamber feed, so that the actual reaction temperature is about 1020°F. The cycle gas heater, vaporizer and superheater coils are all incorporated into a single convection-type gas-fired furnace as indicated in the flow sheet for this process, given in Fig. 37. The vapors from the reaction chamber are scrubbed, bottoms removed, and condensed. The overhead gases are returned as recycle feed. This treatment is said to give little or no coke or carbon.

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[100] R. G. Collins, *Oil & Gas J.*, 1935, **34** (22), 40.

[101] N. Williams, *Oil & Gas J.*, 1935, **34** (25), 38; *J. Inst. Pet. Tech.*, 1936, **22**, 21A; *Chem. Abs.*, 1936, **30**, 1216. W. W. Holland and A. P. Sachs, *World Petroleum*, 1934, **5** (7), 236; *J. Inst. Pet. Tech.*, 1934, **20**, 493A; *Chem. Abs.*, 1934, **28**, 6555. A. P. Sachs, *Petroleum Z.*, 1934 **30** (46), 1; *Chem. Abs.*, 1935, **29**, 3815; *Brit. Chem. Abs.* **B**, 1935, 7. See also G. N. Critchley, *Fuel*, 1934, **13**, 100; *Brit. Chem. Abs.* **B**, 1934, 486; *J. Inst. Pet. Tech.*, 1934, **20**, 363A.

Forward Process. A description of the Forward Process has been given by Kaplan and Forney.[102] In this unit, distillate oil is preheated to 900°F. and passed through a cracking coil (1 inch in diameter and about 2300 feet long), maintained at 1050°F. under a pressure of 225 lbs. per sq. in. The velocity of the gas is arrested in a carbon settling chamber (also kept at 1050-1075°F.). The cracked vapors leaving the top of the chamber are quickly chilled by means of a water spray, condensed and fractionated. Fig. 38 represents a flow diagram for this type of operation. The aromatic content of the gasoline obtained from gas oil charging stock with this method is reported as being about 85 per cent.

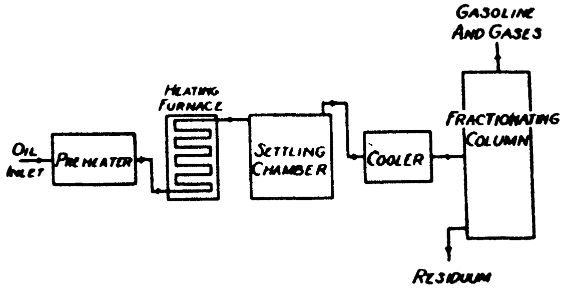

Fig. 38.—Flow Diagram of Forward Vapor Phase Process. (Described by W. Kaplan and W. E. Forney)

Shukhov-Kapelyushnikov Process. The Shukhov-Kapelyushnikov cracking unit is reported to be one of a vapor-phase type in use in U.S.S.R.[103] In this method, gas oil under 15 to 16 atmospheres pressure is forced into a furnace and heated sufficiently so that the temperature in the reaction chamber into which the material is next fed will be 570-580°C. In the latter apparatus the pressure is reduced to 1.5 to 3 atmospheres. The yield of 210°C. end point gasoline is given as 38 to 40 per cent. The refined product is stated to be highly aromatic in character.

Dubrovai Process. In the Dubrovai vapor-phase cracking unit (a flow sheet of which is given in Fig. 41), the stock is preheated to about 400°C. in a tube still and passed into a "generator." In this chamber the temperature of the stock is raised to 500°C. and air is introduced. Cracking takes place and the vapors are fed into a flashing tower, fractionated and condensed. The process operates at atmospheric pressure. In the so-called generator, the cracking temperature is probably considerably lower than is customary with other vapor-phase cracking units, according to Dubrovai and Sheinman.[104] The principal product of combustion is water and only insignificant amounts of carbon monoxide and carbon dioxide are reported to be formed. Carbon is deposited in the generator, however, and is periodically burned out with air. The amount of air used in the cracking process varies from 180 to 240 liters per kilogram of cracking stock, depending upon the preheating temperature and the nature of the feed stock.

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[102] W. Kaplan and W. E. Forney, *Nat. Pet. News*, 1936, **28** (28), 35; *Chem. Abs.*, 1936, **30**, 6175; *Brit. Chem. Abs.* **B**, 1937, 108; *J. Inst. Pet. Tech.*, 1936, **22**, 448A.

[103] B. Kushelevskii, *Neft*, 1932, **3** (9-10), 15; *Chem. Abs.*, 1935, **29**, 2711; *Brit. Chem. Abs.* **B**, 1935, 1030.

Courtesy Doherty Research Co.

FIG. 39.—Preheaters in Forward Process. (W. Kaplan and W. E. Forney)

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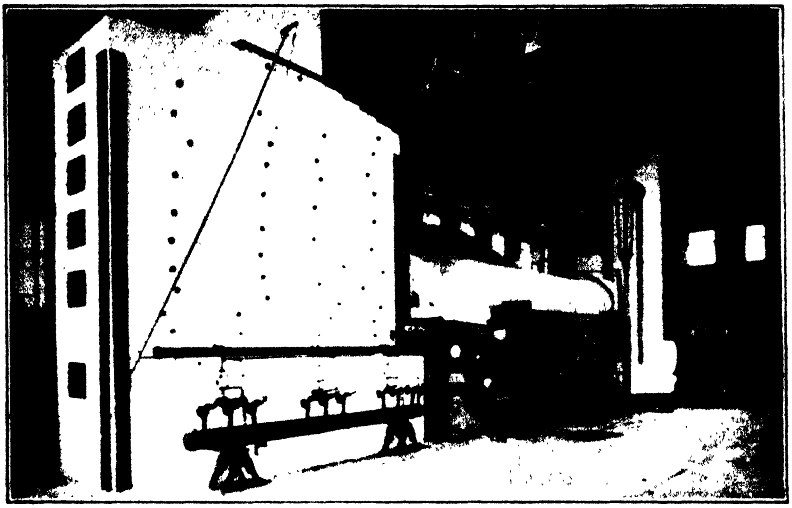
[104] K. K. Dubrovai and A. B. Sheinman, *Trans. 1st All-Union Meeting All-Union Sci.-Eng.-Tech. Soc. Petroleum Workers, Baku, 1933, Gosud. Nauch. Tekh. Gorno-Geol. Neft. Izdat.*, 1934 (3), 4; *Foreign Petroleum Tech.*, 1935, 3, 89; *Chem. Abs.*, 1935, 29, 4558; *Brit. Chem. Abs.* B, 1936, 227.

Clark Process. This vapor-phase process[105] differs from others in that cracking is effected by directly mixing hot products of combustion with superheated oil vapors, rather than by indirect heating, as through steel tubes or other metallic surfaces.[106] In Fig. 42, is a flow sheet for this method. The crude oil is preheated and fed into a fractionating column, from which a gas oil cut is taken off. Part is reintroduced into the tower as controller reflux, and the remainder is pumped directly to a two-stage heater. Here the stock is vaporized at 750°F., passed into a flash drum (to remove unvaporized portions), and the vapors returned to the furnace for superheating to 810°F. The superheated gas oil vapors are now contacted with hot combustion gases at about 1010°F. in a constricted connection between the combustion chamber and the reactor, for a period sufficient to permit cracking to gasoline, without over-cracking and the attendant large gas loss. In the combustion chamber (usually horizontal), heat is produced by burning refinery or stripped gas, pipe line gas, or fuel oil, with the amount of air necessary for complete combustion, under a gage pressure of about 40 lbs. per sq. in. (It is necessary to properly proportion the amounts of fuel and air so as to give a non-coking flame containing no excess oxygen.) The combustion vapors must be oxygen-free or partial oxidation of the charge would occur. After passage through the reactor, the gases are introduced into the fractionating column. The overhead from the column consists of fixed gases and gasoline, which are separated. The bottoms are said to be adaptable as a highway construction material.



Courtesy Doherty Research Co

FIG. 40.—Flash Boiler, Preheaters and Carbon Settling Drum in Forward Process. (W. Kaplan and W. E. Forney)

Houdry Process. The so-called "Houdry Process" is based upon the vapor-phase cracking of crude oils in the presence of a catalyst and was introduced in this country in the latter part of 1930 after being developed in France to some extent.

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[105] L. Clark, U. S. P. 1,491,518, Apr. 22, 1924; *J.S.C.I.*, 1924, **43**, 460B. British P. 132,377, 1918; *J.S.C.I.*, 1919, **38**, 809A U. S. P. 1,989,455, Jan. 29, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 135A; *Chem. Abs.*, 1935, **29**, 1975; *Brit. Chem. Abs.* B, 1935, 1035.

[106] A description of this process has been given by J. C. Albright, *Refiner*, 1935, **14**, 43; *J. Inst. Pet. Tech.*, 1935, **21**, 168A; *Chem. Abs.*, 1935, **29**, 2712.

The advantages of the method of treatment involved in this procedure are said to be in the use of moderate temperatures and pressures and in the formation of a high octane gasoline (75 to 85 octane number, depending upon the charging stock) and a residuum of the gas-oil boiling range. The latter is reported to be applicable as a Diesel fuel or a domestic fuel oil. The untreated gasoline is stated to possess low gum and sulphur contents and high oxygen-bomb stability. The production of gasoline in the Houdry Process is held to be the result solely of catalytic action. This assumption is also evidenced by the products, gasoline, residual oil and gas, which have been found to be quite different in their molecular structure from the corresponding resultants of other processes.[107]

In general, the process is adaptable to a wide range of petroleum distillates which vaporize in the neighborhood of 775° to 875°F. and may be employed in either of two ways. The charging stock may be cracked to a yield of about the same as or slightly higher than that of mixed phase thermal treatments, or it may be run to a 35 to 50 per cent conversion (depending upon the stock) and the residual oil cracked in a separate thermal plant. A catalyst of high activity is used. However, since the catalytic action of the contact mass is greatly lowered due to the deposition of carbonaceous material, a regeneration process is necessary. Each of these factors will now be discussed in more detail.

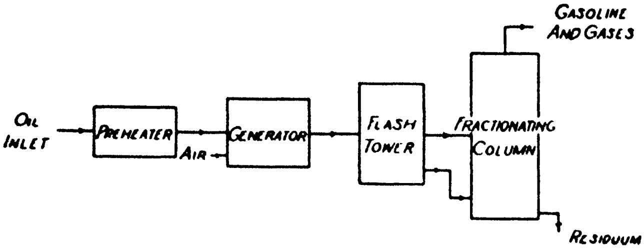

FIG. 41.—Flow Diagram for Vapor Phase Cracking Using Air. (Described by K. K. Dubrovai and A. B. Sheinman)

The Houdry plant embodies standard refinery equipment, except that catalysts cases and a regenerating system must be included.[108] The only important difference is that the catalyst cases are substituted for the reaction chambers. A flow sheet of this type of operation is shown in Fig. 43. Petroleum oil is preheated, mixed with a small quantity of steam and vaporized in the temperature range of 775 to 875°F. and at substantially atmospheric pressure.[109] Joseph[110] has stated that up to 15 per cent of steam may be incorporated with the oils. However, 5 per cent is recommended, as the presence of too large an excess of steam is objectionable, especially in the subsequent distillation of the reaction mixture. (According to Joseph, the steam is not decomposed in this stage and assists only in vaporizing the oil.) The mixture of oil vapor and steam is passed over solid molded catalysts which are contained in cylindrical steel cases, provided with a system for regenerating the catalyst. The product is fed into a fractionating column and the recycle oil removed. Gasoline, fixed gases and steam are cooled and separated and the gasoline recovered from the fixed gases by the conventional methods.

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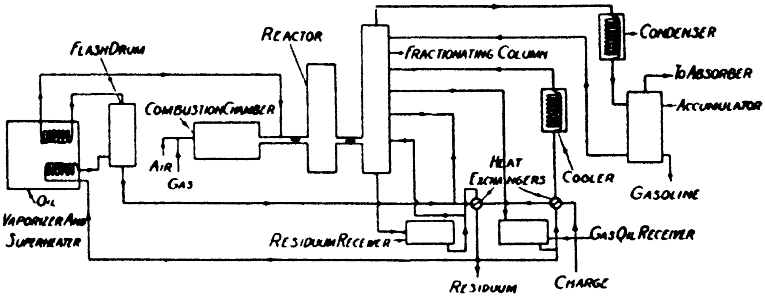
[107] *Oil and Gas J.*, 1933, **32** (22), 12, 31; *Chem. Abs.*, 1934, **28**, 302; *J. Inst. Pet. Tech.*, 1934, **20**, 27A. E. A. Prudhomme, U. S. P. 1,780,536, Nov. 4, 1930, to Soc. internationale des procedes Prudhomme (S. I. P. P.); *Chem. Abs.*, 1931, **25**, 198; *Brit. Chem. Abs.* B, 1931, 529. A. Joseph, U. S. P. 1,867,841 and 1,867,842, June 19, 1932, to Houdry Process Corp.; *Chem. Abs.*, 1932, **26**, 5200. E. J. Houdry, U. S. P. 1,957,648 and 1,957,649, May 8, 1934, to Houdry Process Corp.; *Brit Chem. Abs.* B, 1935, 214; *Chem. Abs.* 1934, **28**, 4217.

[108] Discussions on the type of apparatus and variations in its construction have been given by: A. J. Ostrander, U. S. P. 1,879,635, Sept. 27, 1932, to Houdry Process Corp.; *Chem. Abs.*, 1933, **27**, 210. A. Joseph, U. S. P. 1,957,652, May 8, 1934; *Chem. Abs.*, 1934, **28**, 4215; *J. Inst. Pet. Tech.*, 1934, **20**, 464A. E. J. Houdry, U. S. P. 1,987,903, 1,987,904, 1,987,905, Jan. 15, 1935; *Chem. Abs.*, 1935, **29**, 1289. U. S. P. 1,989,692, Feb. 5, 1935; *Brit. Chem. Abs.* B, 1935, 1072; *J. Inst. Pet. Tech.*, 1935, **21**, 172A; *Chem. Abs.*, 1935, **29**, 1689. U. S. P. 1,989,927, Feb. 5, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 173A; *Chem. Abs.*, 1935, **29**, 1975; *Brit. Chem. Abs.* B, 1935, 1073. J. W. Harrison and R. C. Lassiat, U. S. P. 1,987,934, Jan. 15, 1935; *Chem. Abs.*, 1935, **29**, 1291. J. W. Harrison, U. S. P. 1,987,933, Jan. 15, 1935; *Chem. Abs.*, 1935, **29**, 1291. R. C. Lassiat, U. S. P. 1,989,934 and 1,989,935, Feb. 5, 1935; *Chem. Abs.*, 1935, **29**, 1977; *J. Inst. Pet. Tech.*, 1935, **21**, 173A; *Brit. Chem. Abs.* B, 1935, 1073. E. J. Houdry and R. H. Hammell, U. S. P. 2,045,600, June 30, 1936; *Chem. Abs.*, 1936, **30**, 5469. E. J. Houdry, British P. 407,699, 1934; *J. Inst. Pet. Tech.*, 1934, **20**, 328A; *Brit. Chem. Abs.* B, 1934, 435; *Chem. Abs.*, 1934, **28**, 4943. British P. 414,413, 1934; *J. Inst. Pet. Tech.*, 1934, **20**, 532A; *Chem. Abs.*, 1935, **29**, 565. J. W. Harrison and R. C. Lassiat, British P. 423,866, 1935; *Chem. Abs.*, 1935, **29**, 4216; *Brit. Chem. Abs.* B, 1935, 385. T. B. Prickett and E. J. Houdry British P. 430,174, 1935; *Brit. Chem. Abs.* B, 1935, 754; *J. Inst. Pet. Tech.*, 1935, **21**, 342A; *Chem. Abs.*, 1935, **29**, 7711. Also British P. 426,642, 1935, and 430,312, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 216A, 342A; *Brit. Chem. Abs.* B, 1935, 530, 753; *Chem. Abs.*, 1935, **29**, 6113, 7709. British P. 449,050, 1936; *Chem. Abs.*, 1936, **30**, 7395; *Brit. Chem.*



Courtesy Gulf Publishing Co.

FIG. 42.—Diagrammatic Sketch of Clark Vapor Phase Cracking Process.

As mentioned previously, the activity of the catalyst is greatly decreased by the deposition of carbonaceous material. Therefore, the contact masses can be used for only a limited period of time before the stream of oil vapor and steam is switched to another catalytic chamber. This may be accomplished quite readily by manipulation of the valves as represented in Fig. 43. The regeneration process consists of two steps. The fouled catalyst is first steamed to remove oil vapor and is then regenerated by blowing through it a mixture of air and the products of combustion from other catalyst cases. The regenerating medium enters the chambers at 150°F. and leaves at 1000°F. These temperatures are said to effect complete elimination of sulphur and carbonaceous material and still be well below those at which the contact agent would be depreciated in activity. Continuous operation is secured by providing several catalysts cases, so that some are always "on stream" (in actual operation) while others are being reactivated.

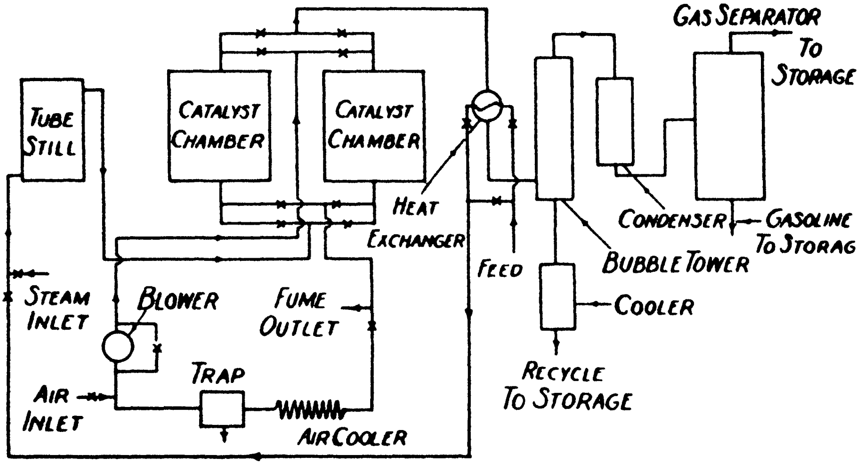
Abs. **B**, 1936, 816. T. B. Prickett and E. J. Houdry, French P. 766,646, 1934; *Chem. Abs.*, 1934, **28**, 7077. E. J. Houdry, U. S. P. 2,072,108, Mar. 2, 1937, to Houdry Process Corp. T. B. Prickett, British P. 456,637, 1936, to Houdry Process Corp.; *Brit. Chem. Abs.* **B**, 1937, 97. U. S. P. 2,062,333, Dec. 1, 1936; *Chem. Abs.*, 1937, **31**, 843. Provisions for utilizing the exothermic heat of reaction in this process are discussed by: A. Joseph, U. S. P. 2,000,960, May 14, 1935; *Chem. Abs.*, 1935, **29**, 4569; *J. Inst. Pet. Tech.*, 1935, 21, 270A. E. J. Houdry, U. S. P. 2,042,468, June 2, 1936; *Chem. Abs.*, 1936, **30**, 4729. British P. 428,416, 1935; *Brit. Chem. Abs.* **B**, 1935, 616; *Chem. Abs.*, 1935, **29**, 7064; *J. Inst. Pet. Tech.*, 1935, **21**, 270A. Also British P. 449,050, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 445A; *Chem. Abs.*, 1936, **30**, 7395.

[109] Cracking must be limited during the vaporization to the extent usually effected in good topping-still operation.

[110] A. Joseph, U. S. P. 2,000,960, May 14, 1935, to Houdry Process Corp.; *Chem. Abs.*, 1935, **29**, 4569; *J. Inst. Pet. Tech.*, 1935, **21**, 270A.

Joseph[111] advocated regeneration by means of a mixture of air or oxygen and steam. Under the conditions generally used, dissociation of the steam gives rise to the formation of oxygen and hydrogen. The oxygen thus set free adds itself to that of the injected air, aiding in burning the carbon to carbon monoxide and carbon dioxide and the sulphur to sulphur dioxide. The nascent hydrogen reduces the sulphur dioxide to hydrogen sulphide and likewise reduces metallic sulphides which might have been formed in the catalytic material.

The catalyst used in the Houdry process must be capable of withstanding the repeated regeneration operations necessary. The contact material generally employed is of the clay type (either natural or synthetic) and is characterized by a high content of silica and alumina, generally in a weight ratio of about 3½ or 4 to 1.



Courtesy Oil and Gas Journal

FIG. 43.—Schematic Representation of Houdry Process.

The clay should contain not more than 10 per cent of iron, calcium and magnesium oxides, and particularly not more than 3 per cent of iron oxide. (The latter substance is thought to have a critical relation to the regenerative operations.) A material which was said to be very satisfactory had the following composition: silica, 76 per cent, alumina, 16.8 per cent, iron oxide, 1.6 per cent, calcium oxide, 2.4 per cent, and magnesium oxide, 1.3 per cent. In making the catalyst, the material is broken up into small fragments, activated by acid treatment, moistened with water or oil, and then molded into a pellet and baked. Promoters, such as nickel, cobalt, copper, manganese, vanadium and molybdenum, may be mixed with the clay prior to the moistening and molding operations.[112]

The preparation of a synthetic contact mass consisting of activated aluminum silicate and a plastic silicate, such as clay, is described by Joseph.[118] Thus, 85 parts of activated aluminum silicate and 12 parts of argillaceous silicate of aluminum are slaked in cold water. Three per cent of alumina (obtained by the action of sodium hydroxide on aluminum sulphate) are added and the resulting material molded into annular pellets (7 to 8 mm. external diameter, 2.5 to 3 mm. internal diameter and 10 to 20 mm. in height) and dried.

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[111] A. Joseph, U. S. P. 1,832,217, Nov. 17, 1931, to Compagnie internationale pour la fabrication des essences et petroles; *Chem. Abs.*, 1932, 26, 838; *Brit. Chem. Abs.* B, 1932, 831.

[112] E. Houdry, British P. 416,025, 1934, to Houdry Process Corp.; *J. Inst. Pet. Tech.*, 1934, 20, 579A; *Brit. Chem. Abs.* B, 1934, 1010; *Chem. Abs.*, 1935, 29, 1220. See also U. S. P. 1,957,648, May 8, 1934; *Chem. Abs.*, 1934, 28, 4217; *Brit. Chem. Abs.* B, 1935, 214.

[113] A. Joseph, U. S. P. 1,837,971, Dec. 22, 1931, to Compagnie internationale pour la fabrication des essences et petroles; *Chem. Abs.*, 1932, 26, 1432.

Houdry[114] has proposed a system of progressive catalytic treatments to effect simultaneous cracking and refining of oils. The oil is vaporized, with steam, and the vapors passed over adsorbent silicates at 550° to 1000°F. In a second chamber, the material is contacted with earthenware fragments (impregnated with nickel or cobalt oxides) at a temperature of 600-800°F. The final operation is carried out at 300-600°F. using an adsorptive silicate impregnated with nickel or cobalt.

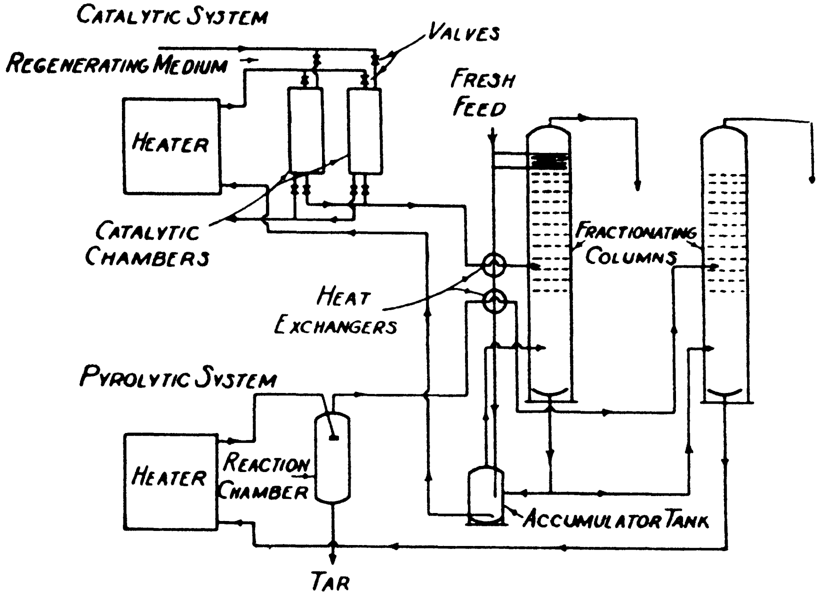

Fig. 44.—Cracking Method Employing Both Catalytic and Thermal Units. (J. P. Daugherty, Jr.)

The residual oils from the Houdry treatment are best cracked in a special unit under separate operations, since successive recycles require differing conditions for best results. These residues have been found to be good feed stocks for thermal units, and so Daugherty[115] has suggested the incorporation of two units, the first of the catalytic type and the second thermal, as shown in Fig. 44. The crude oil is first cracked by the Houdry method and the reaction mixture fractionated in the first column to remove the gasoline portion. The bottoms from this fractionating tower are passed into a second tower (part of the residuum may be diverted into recycle stock for the catalytic system) and then into the heater of the pyrolytic unit, which may be any one of the several types mentioned previously in this chapter. The vapors from the reaction chamber are fed into the second fractionator where additional quantities of gasoline are removed. In this manner, the advantages of both systems may be utilized.[116]

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[114] E. J. Houdry, U. S. P. 1,837,963, Dec. 22, 1931, to Compagnie internationale pour la fabrication des essences et petroles; *Chem. Abs.*, 1932, **26**, 1434. British P. 388,189, 1933, to Houdry Process Corp.; *Chem. Abs.*, 1933, **27**, 4664; *Brit. Chem. Abs.* B, 1933, 340.

[115] J. P. Daugherty, Jr., U. S. P. 2,031,591, Feb. 25, 1936, to Houdry Process Corp.; *J. Inst. Pet. Tech.*, 1936, **22**, 149A; *Chem. Abs.*, 1936, **30**, 2361.

Other Processes. Efforts to increase the quality and yield of the motor fuel produced by cracking have resulted in a number of variations on the procedures mentioned above. Lederer[117] has described the Heckmann process, in which the cracking operation is divided into three stages of sucessively higher, lower and intermediate temperature. In each unit, after the separation of the gasoline and asphalt the middle oil is recirculated. Giordani[118] has discussed the Carburol process which is held to be especially adapted to the production of asphalts as well as gasolines from heavy stocks. In this method, the oil is kept in the cracking zone for 1 to 2 minutes, and secondary reactions are eliminated by sudden cooling. Smith[119] has suggested a two-stage cracking mechanism in which the vapors from liquid-phase operations are subjected to vapor-phase reforming. Likewise the feed stock may be cracked in the vapor phase at 540-675°C. and low pressure. The vapors from this stage are cooled by contact with fresh charging stock, and the latter mixture is fractionated to remove gasoline and fuel oil portions. The residual oil is then subjected to liquid-phase cracking.[120] Holding the cracked oil at a temperature slightly below that used in the cracking operation while still maintaining the high pressure (in order to allow polymerization of the gum forming substances) has also been proposed.[121] Cracking in the presence of recycled gaseous olefins has been stated by Sullivan[122] to improve the quality of the motor fuel. Dilution of the vapor with an inert gas such as nitrogen has been suggested.[123]

Processes involving cracking by means of molten metal as the heating medium have also been proposed. Slowter, Hobart and Withrow[124] have stated that neither tin nor lead has any catalytic effect when compared to ordinary steel heat-transfer surfaces. However, these investigators found that the use of molten metal baths resulted in better heat transfer, more uniformity in temperature control, and a minimizing of coking on the heat-transfer surfaces. According to Garofalo,[125] oils may be cracked in the vapor phase by injecting the hydrocarbon vapors into molten lead.[126] Govers[127] suggests the elimination of secondary cracking reactions by preheating the oil to 400°C. and contacting it with molten lead at 540°C. The

[116] The exhaust gases from the cracking operation may be catalytically polymerized to form gasoline in units similar to those mentioned here. Suggestions for this procedure have been given by E. J. Houdry, U. S. P. 2,035,478, Mar. 31, 1936, to Houdry Process Corp.; *J. Inst. Pet. Tech.*, 1936, **22**, 261A; *Chem. Abs.*, 1936, **30**, 3622. Also British P. 421,650, 1934; *Brit. Chem. Abs.* **B**, 1935, 215; *Chem. Abs.*, 1935, **29**, 3819. W. F. Faragher and E. J. Houdry, Canadian P. 353,825, 1935; *Chem. Abs.*, 1936, **30**, 2747. See also Chapter 26.

[117] E. L. Lederer, *Petroleum Z.*, 1936, **32** (17), 1; *Brit. Chem. Abs.* **B**, 1936, 581; *Chem. Abs.*, 1936, **30**, 7827.

[118] C. Giordani, *Energia termica*, 1935, **3**, 138; *Chim. & ind.*, 1935, **35**, 567; *Chem. Abs.*, 1936, **30**, 3986.

[119] A. D. Smith, U. S. P. 2,035,727, Mar. 31, 1936, to Jenkins Petroleum Process Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 261A; *Chem. Abs.*, 1936, **30**, 3629.

[120] C. B. Watson and C. L. Smith, U. S. P. 2,037,953, April 21, 1936, to Pure Oil Co., *Chem. Abs.*, 1936, **30**, 4000; *J. Inst. Pet. Tech.*, 1936, **22**, 262A.

[121] S. Tijmstra, U. S. P. 1,969,956, Aug. 14, 1934, to Shell Petroleum Corp.; *Chem. Abs.*, 1934, **28**, 6293; *J. Inst. Pet. Tech.*, 1934, **20**, 534A.

[122] F. W. Sullivan, Jr., U. S. P. 2,022,221, Nov. 26, 1935, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1936, **30**, 848; *Brit. Chem. Abs.* **B**, 1936, 777. See also P. H. Sullivan, U. S. P. 2,017,874, Oct. 22, 1935, to Gasoline Products Co.; *Chem. Abs.*, 1936, **30**, 276; *J. Inst. Pet. Tech.*, 1935, **21**, 456A.

[123] E. Moehrle, U. S. P. 1,963,757, June 19, 1934; *Chem. Abs.*, 1934, **28**, 5223; *J. Inst. Pet. Tech.*, 1934, **20**, 501A. See also M. L. Chappell, U. S. P. 1,984,519, Dec. 18, 1934; *Brit. Chem. Abs.* **B**, 1935, 1128; *J. Inst. Pet. Tech.*, 1935, **21**, 97A; *Chem. Abs.*, 1935, **29**, 920.

[124] E. E. Slowter, F. B. Hohart and J. R. Withrow, *Trans. Am. Inst. Chem. Engs.*, 1935, **31**, 698; *Chem. Abs.*, 1936, **30**, 2735.

[125] R. J. Garofalo, U. S. P. 1,948,345, Feb. 20, 1934, to Union Oil Co. of Calif.; *J. Inst. Pet. Tech.*, 1934, **20**, 329A; *Chem. Abs.*, 1934, **28**, 2885.

[126] The use of molten metal baths in cracking is well known. See Carleton Ellis and J. V. Meigs, "Gasoline and Other Motor Fuels." D. Van Nostrand Co., New York, 1921 and Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, 1934.

[127] F. X. Govers, U. S. P. 1,971,748, Aug. 28, 1934, to Indian Refining Co., *Chem. Abs.*, 1934, **28**, 6560; *J. Inst. Pet. Tech.*, 1934, **20**, 579A.

converted oil is immediately removed from the reaction zone and cooled. The cracking reactions are said to occur instantaneously.[128]

Electrical cracking has also been investigated. Fischer, Peters and Winzer[129] have studied the effect of a high tension electric arc on liquid hydrocarbons. The yield of gases was about 4 times that of liquids. Hydrogen was the predominant gaseous product, with acetylene the principal unsaturated constituent. Peters and Winzer[130] have discussed the cracking of Kogasin II[131] using platinum wire and graphite rod electrodes. The data from these tests are incorporated in Table 32.

TABLE 32.—*Cracking of Kogasin II with Graphite and Platinum Electrodes.*

	Graphite Rod	Platinum Wire
Current, amps	14	36
Power, watts	112	730
Duration of test, min.	108	58
Productivity, g./k.w.h.	143.5	295.0
Products, weight %		
Gas	85.3	84.4
Liquid	14.7	15.6
Composition of cracked Gas, volume %		
Unsaturates	69.0	71.6
Hydrogen	12.7	12.1
Saturates	18.3	16.3

The products in each instance are quite similar, and consist mostly of unsaturated gases. Both electrodes became coated with a tight, glossy, thin layer of carbon, and it was thought that the actual decomposition of the hydrocarbons took place on this incandescent graphitic surface and not on the electrode itself. Gobert[132] has obtained 35 to 40 per cent yields of acetylene by cracking heavy oils in an electric arc. Hydrogen, ethylene and small amounts of methane and nitrogen were also formed. The production of 1 cubic meter of gas (containing 40 per cent acetylene) from 800 g. of oil required an energy input of 3.5 kilowatt hours. High boiling tars and oils may be cracked by heating to 200 to 500°C. under 2 to 50 atmospheres pressure when subjected to the influence of high frequency fields.[133] Low frequency currents may also be used for this purpose.[134]

AQUOLIZATION

Aquolization is a process in which hydrocarbon oils are cracked in the vapor phase in the presence of large excesses of steam. Most procedures involving this method of treatment call for ratios of about 18 to 80 moles of water to 1 mole of oil. Using this procedure, polymerization is said to be negligible and, furthermore, there is substantially no coke or tar formation. However, small amounts of water do react with the hydrocarbons to yield aldehydes, alcohols, ketones, acids, and carbon dioxide. The temperature range for aquolysis is from 900 to 1300°F. and the pressure limits usually from 70 to 1000 atmospheres. Ordinarily, pressures in the magnitude of 200 atmospheres are used. The time of contact varies from 0.1 to 2 minutes, depending upon the other factors. The charging stock may be crude oil, fuel oil, gas oil, tars and tarry oils, shale oils and oil emulsions. It is desirable, however, that the water used should be soft in order that mineral matter will not be deposited in the apparatus.

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[128] A. Y. Kubul'nek (*Neft.*, 1933, 4 (5), 22; *Chem. Abs.*, **1935**, 29, 2711; *Brit. Chem. Abs.* **B**, 1935, 1930) has discussed the so-called Phenylic cracking system, which uses a mixture of biphenyl and diphenyl oxide for heating the oil.

[129] F. Fischer, K. Peters and K. Winzer, *Brennstoff-Chem.*, 1935, 16 (22), 421; *J. Inst. Pet. Tech.*, 1936, **22**, 141A. See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**, for a discussion of electrical action on oils.

[130] K. Peters and K. Winzer, *Brennstoff-Chem.*, 1936, 17, 429; *Chem. Abs.*, 1937, **31**, 1990.

[131] Kogasin II is the high-boiling portion of the liquid hydrocarbon mixture obtained in the Fischer-Tropsch process. See Chapter 52.

[132] Gobert, *J. Acetylene*, 1934 (**92**), 948; *Chim. & ind.*, 1935, **33**, 103; *Brit. Chem. Abs.* **B**, 1935, 1052; *Chem. Abs.*, 1935, **29**, 2855.

[133] German P. 595,330, 1935, to Aktis A.-G.; *J. Inst. Pet. Tech.*, 1935, **21**, 420A; *Chem. Abs.*, 1935, **29**, 8316.

[134] J. F. Walt, U. S. P. 1,979,126, Oct. 30, 1934; *Chem. Abs.*, 1935, **29**, 60; *Brit. Chem. Abs.* **B**, 1935, 813.

Ellis[135] has described one procedure (See Fig. 45) in which water and gas oil are forced under a pressure of 3000-3500 lbs. per sq. in. through a heat interchanger and a preheater and into the reaction chamber. In this unit, the reaction mixture is kept at 1000° F. for 20 seconds. The vapors leaving the reaction zone are cooled slightly below the critical temperature (400-500° F.) so that water separates as a liquid phase. Without reduction in pressure, the converted oil is removed from the water, and the latter is recirculated. The product is distilled and subsequently refined. Conversions as high as 75 per cent to motor fuel (boiling below 430-450° F.) have been obtained with this procedure using 4 parts of water to 1 of gas oil. Ammonia may be substituted for water in this process. Haslam[136] has suggested introducing superheated steam into vaporized gas oil and recycling the fixed gases in the system. He also mentions the use of catalysts such as iodine, ferric chloride or the oxides of nitrogen, although this variation is generally unnecessary since the reaction velocity is ordinarily quite fast. According to Haslam, operations carried out at 1200° F. under 3000 lbs. per sq. in. pressure with a reaction time of 13.4 seconds using a mixture of 18 moles of steam to 1 mole of oil resulted in a yield of 72 per cent of high antiknock gasoline. The residue obtained from the treatment was not a heavy tarry mass, as is the usual case in pyrolytic cracking operations, but was very similar to the original gas oil in its appearance.

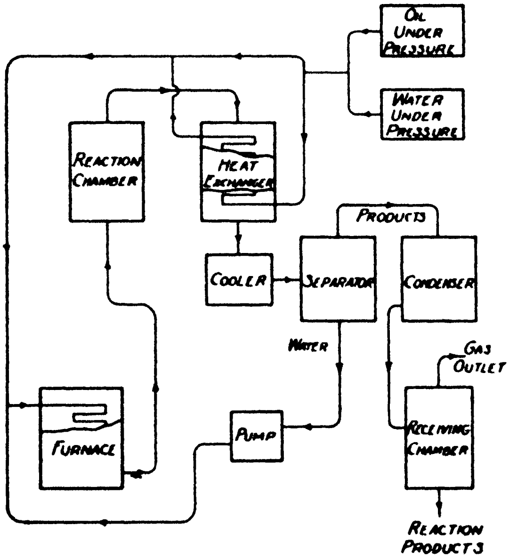

Fig. 45. Aquolization Involving Recycling of Water. (Carleton Ellis)

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[135] Carleton Ellis, U. S. P. 1,956,567. May 1, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1934, 28, 4215; *Brit. Chem. Abs.* B, 1935, 216; *J. Inst. Pet. Tech.*, 1934, 20, 463A.

[136] R. T. Haslam, U. S. P. 1,956,573, May 1, 1934, to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1935, 216; *Chem. Abs.*, 1934, 28, 4215; *J. Inst. Pet. Tech.*, 1934, 20, 463A.

White[137] has investigated the aquolysis of emulsions of both oil-in-water and water-in-oil types. He reports a 92.8 per cent conversion of gas oil to motor fuel boiling below 435°F. by treating an emulsion containing 80 moles of water to 1 mole of gasoline. The exemplified conditions for the aquolization were 1000°F. and 3000 lbs. per sq. in. pressure with a contact time of 65 seconds.

Several variations on the aquolization principle have been proposed. Foss[138] has suggested vaporizing hydrocarbons under pressure and feeding in steam heated to 1200°C. The operations are carried out in a series of tubes which are provided with traps to discharge both liquid and gaseous products. Egloff[139] prefers to add a solution of magnesium chloride to the oil prior to the heating and reaction zones. The magnesium chloride decomposes, forming magnesium hydroxide and hydrochloric acid. By this treatment, the sulphur content of the product is said to be reduced, and at the same time a partial hydrogenation and chlorination of the unstable unsaturated compounds are effected.

Russell[140] advocates agitating oil, water and a gas rich in carbon dioxide to form an emulsion. On contacting this mixture with waste gaseous products of combustion, the oil is cracked. By agitating oxygen with the mixture of oil and water and spraying the emulsion into a heated retort, cracking and partial combustion occur.[141] The resulting vapors are subsequently hydrogenated to form gasoline.

MATERIALS AVAILABLE FOR CONSTRUCTION OF CRACKING EQUIPMENT

The question of materials for the construction of the various parts of cracking units has been discussed by Morrell, Mekler and Egloff.[142] These authorities have pointed out that alloy steels have been in increasing demand in the cracking industry because of the higher operating temperatures now prevalent. To be satisfactory for use in these operations an alloy must possess three major properties: (1) resistance to corrosion of surfaces in contact with the hot oils or vapors undergoing treatment, (2) stability and strength at high temperatures and pressures and (3) resistance to oxidation and the oxides of sulphur on the surfaces directly exposed to combustion gases.

Formerly, stainless steels were employed in handling highly corrosive crudes. However, due to the crystallizing tendency of chromium under high temperatures, these steels become very brittle and therefore unsafe after protracted use. Chromium-nickel steels were next substituted. The stability of the latter type of alloys with regard to heating and cooling has been greatly improved by the addition of small percentages of carbon and molybdenum. Schiffler[143] reported that alloying these steels with 0.05 per cent of molybdenum, 0.1 per cent of vanadium or 0.6 to 0.8 per cent of aluminum improves the heat-resistance properties.

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[137] A. White, U. S. P. 1,956,603, May 1, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1934, **28**, 4215; *J. Inst. Pet. Tech.*, 1934, **20**, 463A; *Brit. Chem. Abs.* **B**, 1935, 216. Also H. O. Forrest, L. F. Marek and A. White, U. S. P. 2,035,120, Mar. 24, 1936, to Standard Oil Development Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 214A; *Chem. Abs.*, 1936, **30**, 3221.

[138] B. Q. P. Foss, U. S. P. 1,982,863, Dec. 4, 1934; *Brit. Chem. Abs.* **B**, 1935, 1126; *Chem. Abs.*, 1935, **29**, 589; *J. Inst. Pet. Tech.*, 1935, **21**, 97A.

[139] G. Egloff, U. S. P. 1,974,301, Sept. 18, 1934, to Universal Oil Products Co.; *Chem. Abs.*, 1934, **28**, 6993; *Brit. Chem. Abs.* **B**, 1935, 759; *J. Inst. Pet. Tech.*, 1934, **20**, 579A. A. Fisher (U. S. P. 2,010,357, Aug. 8, 1935, to Universal Oil Products Co.; *J. Inst. Pet. Tech.*, 1935, **21**, 379A; *Chem. Abs.*, 1935, **29**, 6419) employs zinc chloride in place of the magnesium chloride.

[140] R. H. Russell, U. S. P. 1,970,771, Aug. 21, 1934, to Gas Fuel Corp.; *Chem. Abs.*, 1934, **28**, 6224; *Brit. Chem. Abs.* **B**, 1935, 759; *J. Inst. Pet. Tech.*, 1934, **20**, 578A.

[141] British P. 410,773, 1934, to Gas Fuel Corp.; *J. Inst. Pet. Tech.*, 1934, **20**, 463A; *Brit. Chem. Abs.* **B**, 1934, 790.

[142] J. C. Morrell, L. A. Mekler and G. Egloff, *Oil and Gas J.*, 1935, **34** (5), 50; *Chem. Abs.*, 1935, **29**, 7058. See also G. Egloff, E. E. Crandal and M. M. Doty, "The Cracking Art in 1935," Universal Oil Products Co., Chicago, 1936.

[143] H. J. Schiffler, *Petroleum Z.*, 1934, **30** (21), 1; *J. Inst. Pet. Tech.*, 1934, **20**, 421A.

According to Morrell, Mekler and Egloff, the resistance of alloys to oxidation is determined by the chromium content of the steel. Thus, the higher the percentage of chromium, the lower the amount of oxidation that will take place. However, the economical angle must also be considered so that, in general, low chromium pearlite steels (containing 4 to 6 per cent of chromium) to which molybdenum and titanium have been added to give mechanical stability and strength have found application. Dixon[144] has suggested mixing about 2 per cent of silicon with these steels especially for use with corrosive stocks such as sulphur-containing oils. Chromium steels containing less than 2 per cent nickel have also been employed.[145]

Coating the steels with aluminum (or calorizing, as it is commonly called) has been used extensively to prevent corrosion and oxidation of metallic surfaces. The calorizing coating of aluminum is quite thin (in the magnitude of 0.005 inch ordinarily), so that mechanical cleaning of parts protected in this manner must be avoided. Winkler and Feiler have suggested burning silicon or titanium into the metal as one method of reducing surface corrosion.[146] Likewise, the V2A series of steel alloys (17 to 19 per cent chromium and 8 to 9 per cent nickel) coated with molybdenum have also been reported as effective in withstanding surface action.[147]

Schiffler has recommended the use of nickel-free steels for high pressure units. These alloys contain 8 per cent of chromium and up to 4 per cent of aluminum and 2.5 per cent of copper.[148]

CRACKING OF HEAVY HYDROCARBON FRACTIONS

Numerous investigations have been conducted with the view of obtaining motor fuels and other products of utility from tars and waste materials.[149] Armistead and Ullrich[150] have suggested converting sludge oil into gasoline. In their method the heavy oil is washed with strong sulphuric acid to form a sludge, which is then mixed with water and gas oil in the ratio of 3:1:2, respectively. Live steam is introduced into the mixture to facilitate the separation of the oil and aqueous layers. After settling, the hydrocarbon portion is removed and the diluent oil recovered by distillation. The distillation residue is then subjected to high pressure cracking at about 400°C. to produce motor fuel.

Oils containing large quantities of sulphur may be treated to eliminate the greater part of this element prior to cracking. Stratford[151] has proposed to refine materials such as a high sulphur-content gas oil or reduced crude oil of paraffin base by solvent action. Thus, extraction of the oil with phenol was found to remove most of the sulphur. The gasoline obtained by cracking oil purified in this manner is said to be of very low sulphur content and may be refined readily by means of solid adsorptive catalysts of the clay type.[152] Pelzer prefers to disperse a desulphurizing agent such as lime or copper oxide in the crude oil and subject the mixture to distillation under pressure.[153]

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[144] E. S. Dixon, U. S. P. 1,950,786, Mar. 13, 1934, to Texas Co.; *Chem. Abs.*, 1934, **28**, 3576; *Brit. Chem. Abs.* **B**, 1935, 180.

[145] British P. 404,984, 1934, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech.*, 1934, **20**, 333A; *Brit. Chem. Abs.* **B**, 1934, 310.

[146] F. Winkler and P. Feiler, U. S. P. 2,018,619, Oct. 22, 1935, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech.*, 1935, **21**, 457A. British P. 403,647, 1933; *Brit. Chem. Abs.* **B**, 1934, 310; *J. Inst. Pet. Tech.*, 1934, **20**, 327A.

[147] British P. 408,691, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5467; *Brit. Chem. Abs.* **B**, 1934, 615.

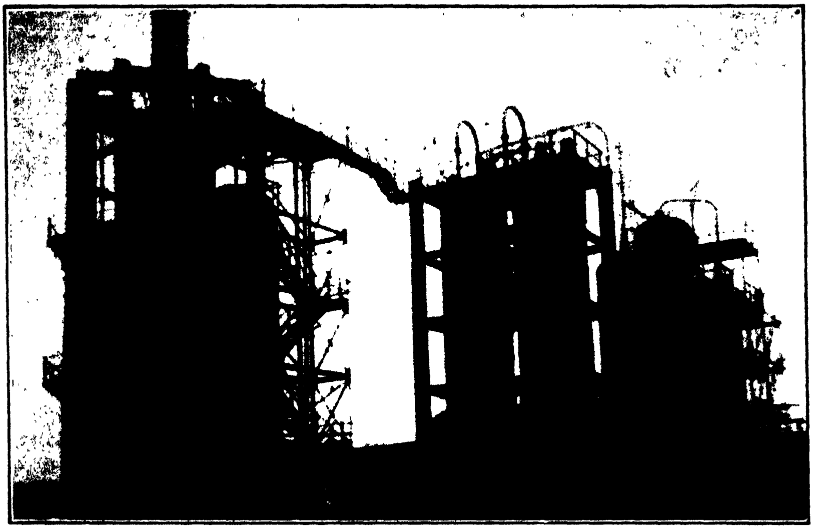
[148] H. J. Schiffler, German P. 622,683, 1935; *Chem. Abs.*, 1936, **30**, 3628.

[149] G. Egloff (*Trans. Fuel Conference, World Power Conference, London (1928)*, 1929, 1, 763; *Chem. Abs.*, 1929, **23**, 4808) has discussed this matter quite comprehensively, summarizing the results obtained in cracking petroleum oils, coal oils, shale oils, bituminous tars and asphalts, wood tars, vegetable oils, fish oils and peat oils.

[150] G. Armistead, Jr., and W. Ullrich, U. S. P. 2,005,309, June 18, 1935, to Texas Co.; *Brit. Chem. Abs.* **B**, 1936, 534; *Chem. Abs.*, 1935, **29**, 5260; *J. Inst. Pet. Tech.*, 1935, **21**, 310A.

[151] R. K. Stratford, U. S. P. 2,007,114, July 2, 1935, to Standard Oil Development Co.; *J. Inst. Pet. Tech.*, 1935, **21**, 379A; *Chem. Abs.*, 1935, **29**, 5645.

The cracking of sapropelite tar at 454°C. and 52 atmospheres pressure is reported to give a gasoline with an initial boiling point of 35 to 40°C.[154] The paraffinic fractions of peat tars have been found to give a yield of 30 to 33 per cent motor fuel in a single vapor-phase cracking operation.[155] Coal tars have been cracked using both vapor-[156] and mixed-phase[157] operations. although, in the latter case, according to Rapoport and Kaftanov,[158] the high yield of coke (about 40 per cent) from certain types of coal tars is objectionable. Gasoline, kerosene and coke are recovered from these tars.[159] The cracking of coking still distillates,[160] shale



Courtesy The Texas Co.

FIG. 45A.—De Florez Cracking Unit.

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[152] G. N. Critchley (*Fuel*, 1934, **13**, 218; *Brit. Chem. Abs.* B, 1934, 787; *J. Inst. Pet. Tech.*, 1934, **20**, 454A; *Chem. Abs.*, 1934, **28**, 7491) has discussed methods of purification of cracked distillates. See Chapter 26 for a discussion of refining by means of clay adsorbents. G. Egloff (U. S. P. 2,009,108, July 23, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 6041; *J. Inst. Pet. Tech.*, 1935, **21**, 379A) and J. C. Morrell and G. Egloff (U. S. P. 2,000,410, May 7, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 4166) have suggested improving the quality of cracked gasolines by the addition of aromatic hydrocarbons and amines. L. Boulanger and F. Emsens (U. S. P. 2,027,464, Jan. 14, 1936; British P. 404,571, 1934; *J. Inst. Pet. Tech.*, 1934, **20**, 327A; 1936, **22**, 148A; *Brit. Chem. Abs.* B, 1934, 310; *Chem. Abs.*, 1936, **30**, 1551) have proposed to remove phenols from cracked oils by mixing the oil vapors with ozone and oxides of nitrogen.

[153] H. L. Pelzer, U. S. P. 2,001,313, May 14, 1935, to Sinclair Refining Co.; *Chem. Abs.*, 1935, **29**, 4569; *J. Inst. Pet. Tech.*, 1935, **21**, 270A.

[154] N. M. Karavaev, I. B. Rapoport and V. I. Karzhev, *Khim. Tverdogo Topliva*, 1931, **2** (3), 22; *Chem. Abs.*, 1934, **28**, 5634.

[155] K. K. Dubroai, *Sotsialist. Rekonstruktsiya i Nauka*, 1935 (2), 168; *Chem. Abs.*, 1935, **29**, 8291.

[156] A. D. Petrov, A. V. Lozovoi and E. A. Pozhiltzeva, *Khim. Tverdogo Topliva*, 1932, **3**, 389; *Chem. Abs.*, 1934, **28**, 5965.

[157] K. Kohlhardt, *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 80; *Chem. Abs.*, 1935, **29**, 8291; *J. Inst. Pet. Tech.*, 1935, **21**, 169A.

[158] I. B. Rapoport and S. V. Kaftanov, *Khim. Tverdogo Topliva*, 1932, **3**, 808; *Chem. Abs.*, 1934, **28**, 5965.

[159] J. C. Morrell and G. Egloff (*Ind. Eng. Chem.*, 1925, **17**, 473; *Chem. Abs.*, 1925, **19**, 1770; *J.S.C.I.*, 1925, **44**, 493B) have also discussed the cracking of low-temperature coal tar.

[160] P. Tarasov, L. A. Aleksandrov and N. V. Popova, *Neft. Khoz.*, 1933, **25**, 100; *Brit. Chem. Abs.* B, 1935, 131; *Chem. Abs.*, 1934, **28**, 4876.

oil,[161] residuum tar,[162] waste rubber[163] and lignite[164] have also been investigated as sources of motor fuels.

The production of motor fuels by the vapor-phase and catalytic cracking of vegetable oils was studied by Koo and Cheng.[165] Vapor-phase cracking of rapeseed oil at 1000°F. yielded 70 per cent of a crude oil, of which 40 per cent boiled below 200°C. Soybean oil, cottonseed oil and China wood oil (tung oil) gave analogous results. Using sodium hydroxide as a catalyst, at 800°F. rapeseed oil formed about 56 per cent of a crude oil, slightly more than half of which boiled in the gasoline range. A kerosene fraction may also be obtained from the crude oil, and by mixing the crude with the vegetable oil, fuel oils stated to be of the Diesel type result.

CRACKING OF MISCELLANEOUS STOCKS

As has been mentioned previously, although the formation of gasoline from higher boiling oils is the chief aim of cracking processes, it is not the only end to which this type of operation may be extended. Numerous applications of the cracking reaction with respect to stocks other than those ordinarily employed will be considered here.

Pyrolysis of a cracking gas (containing 48.6 to 66.7 per cent by weight of reactive hydrocarbons) freed of gasoline fractions has been investigated by Pletnev.[166] By cracking at 5 atmospheres pressure and 625°C. the reactive hydrocarbon content of the exit gas was reduced to 21.2 per cent and at higher temperatures (680°C.) to as low as 1.5 per cent (by weight). Best results were obtained at 660°C. yielding a motor fuel with an octane number of 99.

Kanep[167] studied the cracking of aviation gasoline (boiling range 65° to 100°C.) freed from pentanes, a naphtha fraction (naphthene base, b.p. 95° to 110°C.) and cyclohexane at temperatures of 650°, 700° and 750°C. The gases obtained by cracking the gasoline and cyclohexane at 700°C. contained 4.5 and 7.4 per cent butadiene, respectively. Ethylene, propene, benzene and toluene were formed in the pyrolysis of the gasoline and the naphtha fraction. However, with cyclohexane both propene and toluene were absent from the reaction products. Kanep attributes the high yields of ethylene (20 per cent) observed in the decomposition of the gasoline to the rupture of 5-membered rings.

Candea and Kühn[168] found that by cracking a gasoline fraction (distilling between 35° and 150°C.) at 600°C. a yield of 52 per cent of gas and practically no liquid resulted. By thermally decomposing this material at slightly lower temperatures (550°C.), the olefinic content of the liquid was increased from 7 per cent to 36.5 per cent and the aromatics from 10 to 15.5 per cent. Likewise, cracking kerosene at 650°C. caused the olefinic constituents to increase from 6 per cent to 40 per cent, while the percentage of aromatics in the liquid increased from 14.5 to 20.5. However, under the latter conditions 71 per cent of the kerosene decomposed to gases. At higher temperatures with long periods of contact and catalysts (such as a mixture of nickel, iron, manganese and calcium oxides) these investigators show that complete dissociation to carbon and hydrogen may result. The catalytic cracking of Rumanian kerosene (b.p. 150-300°C.), containing 16 per cent aromatics, 5 per cent unsaturates and 79 per cent paraffins and naphthenes, was investigated by Candea and Sauciuc.[169] In the temperature range of 450-770°C. the maximum yield (49 per cent) of low-boiling hydrocarbons was obtained, using activated carbon as catalyst. With increasing conversions to the lower hydrocarbons, the proportions of olefins and aromatics in the liquid formed also rose. Aluminum silicate especially promoted the production of highly aromatic liquids. Metallic catalysts, such as nickel, however, increased the formation of gases. Kanep[170] has pyrolyzed various kerosene fractions at 700°C. His results indicate that the aromatic content of the cracked liquid decreases with the increased boiling range of the fraction. Thus, the percentage of aromatics produced by cracking the various fractions at 700°C. are:

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[161] T. Mizoshita and M. Ueno. *J. Soc. Chem. Ind., Japan*, 1935. **38**, 248B; *Brit. Chem. Abs.* **B**, 1935, 934; *Chem. Abs.*, 1935. **29**, 6743. A. Fisher and J. C. Morrell. *J.S.C.I.*, 1933, **52**, 228T; *Chem. Abs.*, 1934. **28**, 2156; *Brit. Chem. Abs.* **B**, 1933, 849.

[162] R. E. Burk. U. S. P. 1.963.517, June 19, 1934, to Standard Oil Co. of Ohio; *Chem. Abs.*, 1934. **28**, 5222; *Brit. Chem. Abs.* **B**, 1935, 344. See also K. J. Smith and H. V. Smith, U. S. P. 1.916,026, June 27, 1933, to Skelly Oil Co.; *Brit. Chem. Abs.* **B**, 1934, 309; *Chem. Abs.*, 1933, **27**, 4657.

[163] T. Kato and H. Sameshima. *J. Soc. Chem. Ind. Japan*, 1935, **38**, 596B; *Chem. Abs.*, 1936, **30**, 2041; *Brit. Chem. Abs.* **B**, 1936, 161.

[164] G. F. Michot-Dupont, U. S. P. 1.981,614. Nov. 20. 1934, to Physical Chemistry Research Co.; *Brit. Chem. Abs.* **B**, 1935. 983; *Chem. Abs.*, 1935, **29**, 582.

[165] E. C. Koo and S. Cheng, *Chinese Industry*, 1935. 1, 2021; *Chem. Abs.*, 1936. **30**, 837. See also K. Ping. *J. Chinese Chem. Soc.*, 1935. **3**, 281; *Chem. Abs.*, 1935. **29**, 7683; *Brit. Chem. Abs.* **B**, 1935, 980 and G. Gallo and R. Correlli. *Atti congresso naz. chim. pura applicata*, **1923**, 257; *Chem. Abs.*, 1924. **18**, 2594; *J.S.C.I.*, 1924, **43**, 458B.

[166] K. N. Pletnev, *Novosti Neftererabotki*, 1936. **3** (7). 1; *Chem. Abs.*, 1936, **30**, 6929.

[167] E. K. Kanep. *Materials on Cracking and Chem. Treatment of Products Obtained, Khimteoret (Leningrad)*, 1935, **2**, 74; *Chem. Abs.*, 1935, **29**, 5640; *Brit. Chem. Abs.* **B**, 1936, 484.

[168] C. Candea and J. Kühn. *Bull. sci. ecole polytech. Timisoara*, 1934, **5**, 97; *J. Inst. Pet. Tech.*, 1934, **20**, 446A; *Chem. Abs.*, 1935, **29**, 8304.

Fraction	Aromatics
Below 150°C.	20.9%
150-210°C.	15.6%
210-270°C.	12%
270-300°C.	12%

In the first of these fractions (that boiling below 150°C.), the quantity of benzene formed was greater than that of toluene; however, this condition was reversed in the other fractions. According to Kanep, the yields of aromatics obtained in the cracking of kerosene distillates are dependent upon the type, the lighter kerosenes giving the highest conversion.

Experiments on the pyrolysis of cylinder oil (sp.gr. 0.92) have also been conducted by Kanep.[171] Although the oil was relatively stable at low temperatures, at 600°C. it yielded 83 per cent of vapors. Decomposition was mainly into hydrogen, methane and carbon, with but small quantities of olefins. The yield of butadiene at 650°C. was only 2.5 per cent. Benzene and toluene were produced in about the same molar ratio. However this is attributed to the highly cyclic nature of the oil.

D'yakova and Petrov[172] have investigated the thermal stability of a number of the higher naphthenes in cracking processes. Synthetic decalin, bicyclohexyl, methylisopropylbicyclononane and amylcyclohexane were cracked under ordinary pressure in an atmosphere of nitrogen. Naphthenes, isolated from Grozny non-paraffin oil and from products of olefins cracked under pressure, boiling within the same ranges as the above-mentioned cyclic compounds, were also cracked under the same conditions. From the yield and nature of both the liquids and gases obtained in these treatments, D'yakova and Petrov believe that the naphthenes of the Grozny oil are more closely related to the monocyclic naphthenes with a long side chain rather than to the bicyclic naphthenes of the type of decalin and bicyclohexyl.

[169] C. Candea and L. Sauciuc, *Bull. sci. ecole polytech. Timosoara,* 1935, **6** (1-2), 91; *Chem. Abs.,* 1936, **30**, 2734.

[170] E. K. Kanep, *Materials on Cracking and Chem. Treatment of Products Obtained, Khimteoret (Leningrad),* 1935, **2**, 71; *Chem. Abs.,* 1935, **29**, 5640.

[171] E. K. Kanep, *Materials on Cracking and Chem. Treatment of Products Obtained, Khimteoret (Leningrad),* 1935, **2**, 90; *Chem. Abs.,* 1935, **29**, 6030; *Brit. Chem. Abs.* **B**, 1936, 676.

[172] M. K. D'yakova and A. D. Petrov, *J. Gen. Chem. (U.S.S.R.),* 1933, **3**, 679; *Chem. Abs.,* 1934, **28**, 3567.

TABLE 33.—*Yields of Products and Gas Analysis from Vapor-*

	Gasoline Midcontinent	Naphtha Midcontinent	Kerosene Midcontinent	Distillate California 1	Distillate California 2
Temperature, °F.	950	975	950	950	950
Pressure, lbs./sq. in.	400	750	400	500	500
Yields:					
Gasoline, % of charge	76.8	52.0	70.6	72.3	61.5
Octane number of gasoline, C. F. R. method	88	104	82	80	83
Residue (liquid), % of charge	6.8	6.0	14.6	9.7	14.7
Gas and loss, % of charge	16.4	43.0	14.8	18.0	23.8
Gas, cu. ft./bbl. charge	483	1182	694	636	625
Gas analysis, % by volume:					
Methane + uncondensables	56.0	60.2	53.0	50.4	73.0
Ethylene	3.6	4.0	4.4	3.4	2.7
Ethane	18.6	8.2	20.6	11.1	11.5
Propene	9.5	5.2	7.0	17.8	5.6
Propane	5.1	10.5	8.7	6.6	3.2
Butenes	1.2	5.1	1.9	7.6	2.6
Butanes	2.4	3.4	3.1	—	—
Butadiene	1.2	—	—	—	—
Pentane and higher	2.4	3.3	9.1	1.8	0.5
Acetylene	—	—	—	1.3	0.9
Total unsaturates	15.5	14.3	13.3	—	—

The cracking of Grozny paraffin (m.p. 53.2°C.) has been studied by Katzman.[173] This material was fairly stable at 600-640°C., only small amounts of benzene (C_6H_6) being formed. At 650°C., however, more than 65 per cent of the paraffin was converted into gases (principally ethylene and propene). In addition, a 2.5 per cent yield of butadiene and a large yield of benzene but only a small amount of high boiling fractions were obtained under these conditions. The effect of the pressure of different gases on the cracking of solid paraffin wax has been noted by Weinstein.[174] At 440°C. under a pressure of 70 to 80 kg. per sq. cm. of nitrogen, the cracking of high molecular weight saturated hydrocarbons resembles closely the analogous reaction carried out with the same substances under reduced pressure. When hydrogen is substituted for nitrogen under the same conditions of temperature and pressure, much less decomposition occurs as is evidenced by the gases evolved and the quantity of liquid boiling below 230°C. Weinstein concludes that the effect of hydrogen is specific and is not common to gases which in general are classed as inert. The effect of the pressure of hydrogen on the production of cyclic compounds in cracking Rangoon paraffin wax at high temperatures has been discussed by Waterman, Leendertse, Adam and van Vlodrop.[175] When the paraffin was cracked thermally, in the absence of hydrogen, the average number of rings produced per mole of wax was 1.6 to 1.7. Under high pressure of hydrogen, however, the average number of rings formed per molecule of wax decomposed was reduced to only 0.4 to 0.5. Using hydrogen in the presence of nickel or kieselguhr, the ring formation was completely prevented.[176]

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[173] S. V. Katzman, *Materials on Cracking and Chem. Treatment of Products Obtained, Khimteoret (Leningrad)*, 1935, 2, 93; *Chem. Abs.*, 1935, 29, 6031; *Brit. Chem. Abs.* B, 1936, 676.

[174] O. Weinstein, *Mitt. Kohlenforschungsinst. Prag*, 1933, 1, 437; *Chem. Abs.*, 1934, 28, 5972; *Brit. Chem. Abs.* B, 1934, 228.

[175] H. I. Waterman, J. J. Leendertse, L. Adam and C. van Vlodrop, *J. Inst. Pet. Tech.*, 1935, 21, 959; *Chem. Abs.*, 1936, 30, 2738; *J. Inst. Pet. Tech.*, 1936, 22, 19A.

[176] For particulars on hydrogenation of petroleum see Carleton Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., Inc., New York, 1930.

Liquid Phase Cracking Tests on Various Petroleum Fractions.

Heavy Naphtha and Lt. Gas Oil	Gas Oils			Topped Crude Oils		Crude Oils	
Calif.	Calif.	Coastal	East Texas	Midcontinent	Somerset	Mt. Pleasant	Refugio
950	950	910	950	950	925	935	930
400	350	400	350	250	250	350	350
70.7	63.2	60.4	60.4	63.4	69.4	69.5	60.1
78	79	89	74	72	73	62	89
15.5	28.2	21.6	26.2	23.5	0.0	20.0	31.3
13.8	8.6	18.0	13.4	13.1	30.6	10.5	8.6
570	495	460	489	531	794	307	382
46.8	44.8	52.1	39.2	39.4	41.3	26.0	60.4
3.4	4.0	3.1	3.9	4.7	4.3	4.8	6.2
18.0	16.2	15.8	21.0	19.7	21.6	16.8	13.4
13.5	14.2	8.7	7.4	9.5	15.4	23.3	7.1
5.7	7.4	9.5	16.2	12.0	6.2	5.4	6.2
2.2	6.0	8.0	2.6	3.0	4.1	17.8	2.4
4.1	—	—	2.3	4.1	3.1	—	—
1.6	4.0	—	4.2	1.9	1.7	—	—
4.7	3.4	2.8	3.2	3.6	2 3	5.4	3.3
—	—	—	—	—	—	0.5	0.9
20.5	22.2	—	24.9	21.2	25.5	—	—

PRODUCTS OF COMMERCIAL CRACKING PROCESSES

The products obtained in commercial cracking processes may broadly be classified as gases, liquids and coke. Both the quantity and composition of all three of these substances vary considerably, depending not only upon the operating conditions of temperature, pressure and heating time, but also upon the charging stock and type of plant. Because of the enormous scale upon which cracking is conducted and, furthermore, because of the increasing demand for higher quality gasoline, a knowledge of the composition of the hydrocarbons formed in the cracking reactions is very important. Unfortunately, because of the complexity of the problem of determining the almost innumerable constituents of these resultants, complete information is not on hand. However, from the general trend of the data available, the composition of these cracked petroleum hydrocarbons may be roughly indicated.[177]

COMPOSITION OF CRACKED GASES

The factors determining the amount and composition of gases formed in cracking are the four fundamental variables;- temperature, pressure, time and composition of feed stock. Egloff and Morrell[178] have studied the cracking of various oils in the commercial production of gasoline from the viewpoint of gas formation and gas composition. Their tests were made using a vapor-liquid phase system with operating conditions of 250 to 750 lbs. per sq. in. pressure and temperatures ranging from 875-975°F. (468-524°C.). The feed stocks included Midcontinent gasoline, naphtha and kerosene, California kerosene, mixed heavy naphtha and light gas oil and gas oil, Coastal and East Texas gas oils, Midcontinent and Somerset topped crudes and Mt. Pleasant and Refugio crude oils. The resultants in these cracking operations were gasoline (from 52 to 76.8 per cent of the charge), flashed liquid residue (up to 47.1 per cent of charge), and gas (from 164 to 1182 cu. ft. per barrel of oil). In the case of the Somerset topped crude, however, the cracking was allowed to go to gasoline, gas and coke. The conditions of these tests, yields and gas analysis are included in Table 33. In every one of these tests, it will be noted that methane and other uncondensable gases formed the bulk of the gas. The other principal constituents in the descending order of amounts produced are ethane, propene, propane and ethylene. The quantity of acetylene obtained is quite small.

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[177] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[178] G. Egloff and J. C. Morrell, *Ind. Eng. Chem.*, 1934, 26, 940; *Chem. Abs.*, 1934, 28, 6988; *Brit. Chem. Abs.* B, 1934, 1044; *J. Inst. Pet. Tech.*, 1934, 20, 527A.

Markovich[179] has correlated data on the composition of the gases obtained in vapor-liquid and vapor-phase cracking as well as cracked gases from petroleum stills. Although the composition of the exit gases varies greatly with the operating conditions (especially in mixed-phase processes), Markovich states that these average values (as given in Table 34) are fairly representative. Thus the differentiation he makes between vapor-phase and mixed-phase cracked gases is that the former are of high olefinic content (about 45 per cent) whereas the latter are practically paraffinic (about 72 per cent total saturated hydrocarbons). The nature of the cracked gas from the distillation operations and that from vapor-phase cracking are quite similar.

TABLE 34.—*Average Composition of Cracked Gases.*

	Liquid-Vapor Phase	Vapor Phase	Still
Hydrogen	3	9	12
Methane	50	28	56
Ethane	17	14	
Propane	10	3	
Butane	5	1	
Higher paraffins	—	—	0.4
Ethylene	2	20	16.3
Propene	9	15	9.0
Butene	4	5	1.6
Isobutene	—	3.5	2.4
Butadiene	—	1.5	1.6
Higher olefins	—	—	1.2

Vapor-phase cracking with specific reference to the gases formed has also been investigated by Otsuka.[180] His experiments were carried out with gas oil at temperatures of 550-750°C. and pressures of about 720 mm. At 550°C., neither hydrogen nor methane was produced, however as the temperature was increased, the formation of hydrogen increased at a fairly rapid rate while that of methane increased very rapidly. Ethane, propane, ethylene and propene and smaller amounts of *n*- and isobutene were present in the gas formed at low temperatures. The maximum value of the C_4 fraction (mainly butenes) was obtained by cracking at 600°C., at which temperature the ethylene formation was a minimum.

NATURE OF LIQUID PRODUCTS OF CRACKING REACTIONS

As might be expected, the composition of the liquid products also varies greatly with the conditions of cracking. Thus, Otsuka[181] has shown that in vapor-phase cracking in the range of 550-700°C. (1020-1290°F.), the sum of the weight percentages of aromatic and olefinic hydrocarbons remains almost constant. At 750°C., however, dehydrogenation of the naphthenes and decomposition of the paraffins to form aromatics become predominant.

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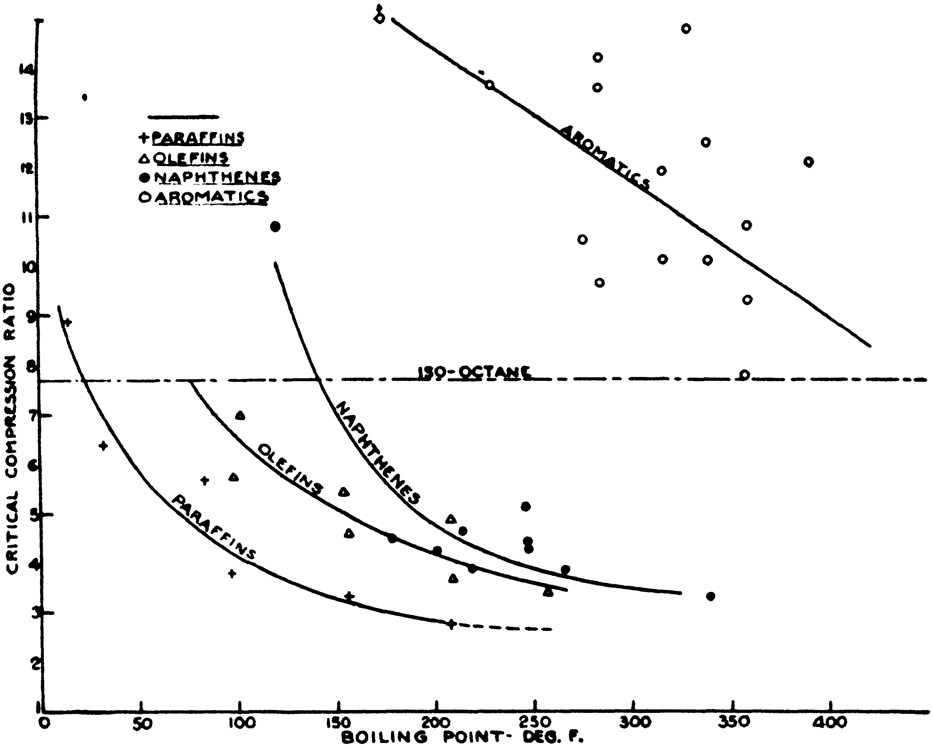
[179] M. B. Markovich, *Materials on Cracking and Chem. Treatment of Products Obtained*, *Goshimtekhizdat (Leningrad)*, 1933, 1, 38; *Chem. Abs.*, 1935, 29, 2712; *Brit. Chem. Abs.* B, 1935, 1030. See also M. Kapelyushnikov, *Azer. Neft. Khoz.*, 1933 (6-7), 138; *Chem. Abs.*, 1934, 28, 7499.

[180] H. Otsuka, *J. Soc. Chem. Ind., Japan*, 1934, 37, 183 (Suppl. bind.); 1935, 38, 305 (Suppl. bind.); *Chem. Abs.*, 1934, 28, 5644; 1935, 29, 6744; *Brit. Chem. Abs.* B, 1934, 707; 1935, 886. *J. Fuel Soc. Japan*, 1936, 15 (165), 59; *J. Inst. Pet. Tech.*, 1936, 22, 504A.

[181] H. Otsuka, *loc. cit.*

The relationship between antiknock rating (expressed as the octane number) and the structure of the hydrocarbon has been discussed by Kaplan and Forney.[182]



Courtesy National Petroleum News

FIG. 46.—Relationship Between Antiknock Properties and Boiling Points of Hydrocarbons. (W. Kaplan and W. E. Forney)

Fig. 46 shows the relation between the critical compression ratio [a function of the antiknock value[183]] and the boiling points of the various classes of hydrocarbons with isooctane as standard. Thus, the lower paraffins possess good antiknock qualities, but this property drops off in the higher members of the series. The olefins as a class possess better antiknock qualities than the paraffins, but, in this case, their stability is a factor which must also be considered. The naphthenes allow the use of higher compression ratios and at the same time are stable chemically. The higher boiling members of all three of these series are very much inferior in their detonating characteristics to isooctane. The aromatics, however, are characterized by an exceptionally high antiknock rating, exceeding even that of isooctane. Despite this quality, Kaplan and Forney state that motor benzol (which contains principally benzene) is undesirable in itself as a motor fuel because, due to its narrow boiling range, it does not allow smooth motor operation under constantly varying conditions.[184] Furthermore, benzene possesses too high a freezing point. Thus, it will be seen that the octane number alone does not determine the usefulness of a cracked product as a motor fuel.[185]

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[182] W. Kaplan and W. E. Forney, *Nat. Pet. News*, 1936, **28** (28), 35; *Chem. Abs.*, 1936, **30**, 6175; *J. Inst. Pet. Tech.*, 1936, **22**, 448A.

[183] See Chapter 44 for a discussion of this relationship.

TABLE 35.—*Composition of Cracked Gasolines.*

	Reforming Straight-Run Gasoline		Cracking Gas Oil	
	Vapor-Phase Cracking[a]	Mixed-Phase Cracking[b]	Vapor-Phase Cracking[c]	Mixed-Phase Cracking[d]
Operating Conditions:				
Temperature, °F.	1060-1080	930	1050	750
Pressure, Atmospheres	1.5-3.0	53	15	18
Yield of Gasoline, %	—	65-70	51.6	32.6
Octane Number of Gasoline	110	80	—	—
Initial B. P., °F.	—	117	133	—
End B. P., °F.	—	392	399	—
Composition of Gasoline, %				
Paraffins	2	33-34.6	0	58-62
Olefins	20	19.3-25.6	4.8-8.6	15-20
Naphthenes	5	18.1-20.9	0-9.8	0-8
Aromatics	73	28-28.9	85.4-91.4	13-20

[a] I. Andreev, *Neft.*, 1934, **5** (5), 9; *J. Inst. Pet. Tech.*, 1936, **22**, 260A.

[b] L. A. Aleksandrov and P. A. Sentzov, *Neft. Khoz.*, 1934, **26** (10), 32; *Foreign Petroleum Tech.*, 1935, **3**, 73; *Chem. Abs.*, 1935, **29**, 2712; *Brit. Chem. Abs.* **B**, 1935, 1030.

[c] W. Kaplan and W. E. Forney, *loc. cit.*

[d] E. Berl and W. Dienst, *Petroleum Z.*, 1933, **29** (32), 1; *Chem. Abs.*, 1934, **28**, 301; *Brit. Chem. Abs.* **B**, 1933, 900.

TABLE 36.—*Effect of Type of Charging Stock and Operating*

	Naphtha Distillate			
Analysis of Charging Stock:				
Gravity, °A.P.I.	55.2			
Initial B.P., °F.	254			
End B.P., °F.	407			
Composition, %:				
Unsaturates	3.9			
Aromatics	0.1			
Naphthenes and Paraffins	96.0			
Cracking Conditions:				
Average Reaction Temperature, °F.	900	1000	1100	1200
Time of Contact, sec.	68	63	59	56
Products Formed:				
Gasoline, %	72.8	69.7	32.2	20.9
Gravity, °A.P.I.	54.5	55.5	48.7	41.2
Coke, lbs./bbl.	None	0.32	0.38	2.4
Gas, cu. ft./bbl.	None	632	1800	2320
Composition of Gasoline, %:				
Unsaturates	7.8	20.1	34.7	36.1
Aromatics	9.4	13.6	36.5	63.9
Napthenes	—	—	5.8	—
Paraffins	82.8	66.3	23.0	—

[184] In this respect, B. K. Tarasov and V. P. Govakov (*Grosnenskii Neftyanik*, 1934, **4** (6-7), 33; *Chem. Abs.*, 1935, **29**, 2716; *Brit. Chem. Abs.* **B**, 1935, 1030) have shown that mixed-phase cracked gasolines give a very irregular octane equivalent curve on being broken up into 5°C. fractions.

[185] G. G. Brown and S. C. Singer, Jr. (*Nat. Pet. News*, 1934, **26** (23), 21; *Oil and Gas J.*, 1934, **33** (10), 80; *Brit. Chem. Abs.* **B**, 1935, 212; *Chem. Abs.*, 1934, **28**, 6990) have stated that gasoline mileage depends upon the heating value per gallon rather than the octane number. According to G. Egloff (*Refiner*, 1935, **14**, 8306; *Chem. Abs.*, 1935, **29**, 8306) cracked fuel contains about 5 per cent more B.t.u. per gallon than the corresponding straight-run fuels.

Table 35 shows the composition of various cracked gasolines and the conditions under which they were produced. The low yields of paraffins and naphthenes and high yields of aromatics both in reforming straight-run gasoline and in cracking gas oil in vapor-phase processes are characteristic.

The researches of Morrell and Egloff[186] on the effect of cracking on the group composition of hydrocarbon distillates are summarized in Table 36. The feed stocks varied from non-aromatic (Pennsylvania naphtha distillate) to high aromatic (pressure distillate bottoms derived from Midcontinent crude oil) in character. The kerosene distillate and straight-run gas oil were also derived from a Midcontinental crude oil. Cracking operations were carried out in the vapor-phase with temperatures ranging from 900° to 1300°F. (480-705°C.). From the data it will be seen that an increase in the reaction temperature causes an increase in the aromatic and olefinic content of the gasoline formed from all of the charging stocks. At the same time, the coke and gas production also rises with elevation in temperatures. Above 1200°F. paraffins and naphthenes are entirely absent in the cracked hydrocarbons.

Zelinskii and Levina[187] have stated that gasolines produced by vapor-phase methods have a total cyclic content (naphthenes and aromatics) of twice that of products from mixed-phase operations (70 to 80 per cent and 30 to 40 per cent, respectively). Butkov and Ostrovai[188] obtained a 14.5 per cent conversion to gasolines of an aromatic content of 94.3 per cent by cracking Baku gas oil at 675°C. (1250°F.) and atmospheric pressure. These investigators stated that by recycling the residual oil, both the yield and aromatic content of the motor fuel may be increased.

The low temperature carbonization of Barzass sapropelites is reported by Kuruindin and Ivanov[189] to result in a high octane number gasoline. The product

Conditions on Gasoline Produced in Vapor-phase Cracking.

Kerosene Distillate				Virgin Gas Oil				Pressure Distillate Bottoms			
36.7				31.7				37.8			
375				406				376			
715				810				681			
3.7				6.9				3.5			
12.6				19.5				24.6			
83.7				73.6				71.9			
900	1000	1100	1200	900	1000	1100	1300	900	1000	1100	1300
160	148	138	129	149	138	129	114	160	148	138	129
17.8	31.5	23.0	17.5	14.5	28.0	23.6	15.2	14.5	29.3	23.7	15.1
51.8	52.3	44.2	36.7	55.4	52.9	42.9	31.9	48.5	50.0	44.6	32.0
None	0.29	1.5	3.6	1.4	1.5	3.2	10.0	None	0.44	1.2	8.6
98	280	1727	2170	134	795	1800	2800	None	383	1463	2492
44.1	52.0	54.6	42.4	53.9	63.6	48.0	17.2	44.6	59.1	56.2	19.4
25.7	25.0	45.4	57.6	32.2	36.4	52.0	82.8	23.8	26.6	43.8	80.6
4.4	6.0	—	—	11.9	—	—	—	4.2	5.7	—	—
25.8	17.0	—	—	2.0	—	—	—	27.4	8.6	—	—

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[186] J. C. Morrell and G. Egloff, paper presented before the Petroleum Division of the American Chemical Society, Pittsburgh Meeting, Sept. 7-11, 1936.

[187] N. D. Zelinskii and R. Y. Levina, *Neft. Khoz.*, 1935, **26** (9), 47; *Foreign Petroleum Tech.*, 1935, **3**, 177; *Chem. Abs.*, 1935, **29**, 4927; *Brit. Chem. Abs.* **B**, 1936, 403.

[188] N. A. Butkov and E. Y. Ostrovai, *Neft. Khoz.*, 1934, **26** (2), 40; *Chem. Abs.*, 1934, **28**, 7499.

[189] K. S. Guruindin and I. I. Ivanov, *Khim. Tverdogo Topliva*, 1932, **3**, 701; *Chem. Abs.*, 1934, **28**, 5633.

is predominantly olefinic (44 to 48 per cent). The proportions of the other types of hydrocarbons are paraffins, 25 per cent, naphthenes, 5 per cent, and aromatics, 22 to 26 per cent.

CHEMICAL CONSTITUENTS OF LIQUID PRODUCTS OF CRACKING

The individual hydrocarbons present in gasoline are extremely numerous and vary with the methods used in cracking the original stock. Moor and Katzman[190] investigated the low-boiling fraction (30 to 45°C.) obtained by the distillation of a gasoline produced by vapor-phase cracking at 570°C. This fraction consisted principally of isomeric pentenes, of which trimethylethylene (2,2-dimethylpropene) and possibly small amounts of *unsym.*-methylethylethylene (2-methyl-1-butene) comprised 17 per cent and 2-pentene and 1-pentene totaled 42 per cent. In addition, 6 to 8 per cent of cyclopentadiene, 10 to 12 per cent of isoprene (2-methyl-1,3-butadiene) and 3 to 7 per cent of piperylene (1,4-pentadiene) were also believed to be present. In this connection, it is interesting to note that Kazanskii, Plate and Artyunyan[191] obtained approximately the same results in their examination of the liquid residue remaining from the distillation of butadiene obtained by cracking kerosene. The portion of this residue boiling between 30° and 52°C. (amounting to 3 per cent of the total) was a mixture of pentenes, piperylene, and possibly isoprene. The other identified components of the residue were: benzene, 55 per cent; toluene, 9 per cent; and cyclopentadiene, 12 per cent.

Potolovskii and Prozumentik[192] have analyzed gasoline recovered from cracked gas and report the following constituents, in per cent: butane and butenes, 10; pentane and pentenes, 20; hexane and hexenes, 12, and higher hydrocarbons, about 58. The composition of the gasoline produced by cracking sapropelite tar has been discussed by Karavaev, Rapoport and Bashkirov.[193] These observers fractionated the gasoline into very narrow cuts and found the following substances: pentane, hexane, heptane, octane, hexene, heptene, octene, nonene, decene, undecene ($C_{11}H_{22}$), cyclohexane, methylcyclohexane, 1,4-dimethylcyclohexane, benzene, toluene and *o*- and *m*-xylenes. Besides the 4 aromatics just mentioned, Kaplan and Forney[194] suggest the inclusion of the following aromatic hydrocarbons: *n*-propylbenzene, isopropylbenzene, *n*-butylbenzene, *sec*-butylbenzene, isobutylbenzene, *n*-amylbenzene, isoamylbenzene, *o*- and *p*-methylethylbenzene, *o*- and *p*-diethylbenzene, *o*- and *p*-methylisopropylbenzene, mesitylene (1,3,5-trimethylbenzene), pseudocumene (1,3,4-trimethylbenzene) and naphthalene. The presence of these hydrocarbons was indicated by the boiling point, specific gravity, refractive index, and molecular weight determinations made on cuts of 5°F. boiling range. The gasoline used for the tests was obtained by the vapor-phase cracking of gas oil. Kuruindin and Shumilov[195] report the presence of cumarone (4.3 per cent)

[190] V. G. Moor and S. V. Katzman, *Materials on Cracking and Chem. Treatment of Products Obtained, Goskhimtekhizdat (Leningrad)*, 1933, 1, 111; *Chem. Abs.*, 1935, **29**, 2717; *Brit. Chem. Abs.* **B**, 1935, 1031.

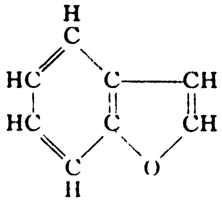
[191] B. A. Kazanskii, A. F. Plate and S. S. Artyunyan, *Sintet. Kauchuk*, 1933 (3), 13; *Chem. Abs.*, 1934, **28**, 3567; *Brit. Chem. Abs.* **B**, 1934, 866.

[192] L. Potolovskii and M. Prozumentik, *Azer. Neft. Khoz.*, 1934 (1), 60; *Chem. Abs.*, 1934, **28**, 7503; *J. Inst. Pet. Tech.*, 1935, **21**, 143A.

[193] N. M. Karavaev, I. B. Rapoport and A. N. Bashkirov, *Khim. Tverdogo Topliva*, 1930, 1 (6), 29; 1931, 2 (9), 46; *Chem. Abs.*, 1934, **28**, 5633, 6281.

[194] W. Kaplan and W. E. Forney, *Nat. Pet. News*, 1936, **28** (28), 35; *Chem. Abs.*, 1936, **30**, 6175; *J. Inst. Pet. Tech.*, 1936, **22**, 448A.

[195] K. S. Kuruindin and A. I. Shumilov, *Khim. Tverdogo Topliva*, 1934, 5, 74; *Chem. Abs.*, 1934, **28**, 6281.



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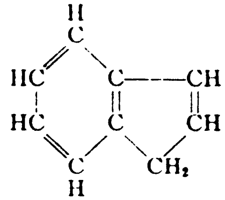

in the 150-175°C. fraction of a gasoline obtained in the distillation of Cheremkhov coal tar.

Undecene ($C_{11}H_{22}$), dodecene, tridecene, tetradecene, heptadecene and octadecene ($C_{18}H_{36}$) have been identified in the kerosene fractions of Barzass sapropelite tar, according to Karavaev and Karzhev.[196] Karavaev, Rapoport and Kholler[197] have isolated acids from formic up to propionic among the liquids obtained by the dry-distillation of these same tars. From the boiling points and esterification values of the methyl esters, the evidence of several higher acids is also indicated. Charrin[198] has reported phenols, paraffin wax, asphalt and pyridine bases in the tar obtained from Creveney pyroschists.

Chemical Composition of Coke

The significance of coke formation and an explanation of the mechanism have already been considered in this chapter. However, the nature of petroleum coke is such as to merit a brief discussion. Petroleum coke is not elementary carbon but consists of complex, high-molecular weight hydrocarbons containing small percentages of hydrogen. According to Trusty,[199] carbon disulphide will dissolve about 50 per cent of most cokes. Aromatic compounds such as anthracene, phenanthrene, chrysene, picene and crakene ($C_{24}H_{18}$) have been identified as constituents in various petroleum cokes. The structures of some of these compounds are shown below. As an example of the degree of unsaturation, picene, for instance, is 95 per cent carbon and 5 per cent hydrogen. The cokes thus resemble the tars from cracking stills in their general nature. The same types of compounds are formed in these two products, but in the former case the hydrocarbons are in a more condensed form.

Ginzburg[200] gives the proximate analysis of coke obtained from heavy bottoms as 0.84 per cent ash and 5 to 6 per cent volatile matter.

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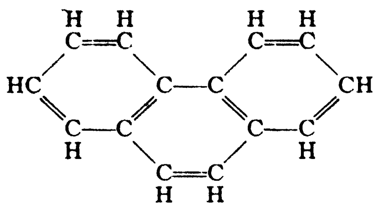
[196] N. M. Karavaev and V. I. Karzhev, *Khim. Tverdogo Topliva*, 1931, **2** (8), 34; *Chem. Abs.*, 1934, **28**, 5636.

[197] N. M. Karavaev, I. B. Rapoport and V. A. Kholler, *Khim. Tverdogo Topliva*, 1930, 1 (4), 27; *Chem. Abs.*, 1934, **28**, 5633.

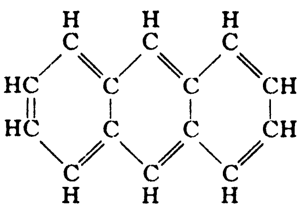
[198] V. Charrin, *Mat. grasses*, 1934, **309**, 10.056; **310**, 10.084; *J. Inst. Pet. Tech.*, 1934, **20**, 320A; *Brit. Chem. Abs.* **B**, 1936, 773.

[199] A. W. Trusty, *Nat. Pet. News*, 1935, **27** (45), 34; *Chem. Abs.*, 1936, **30**, 2734.

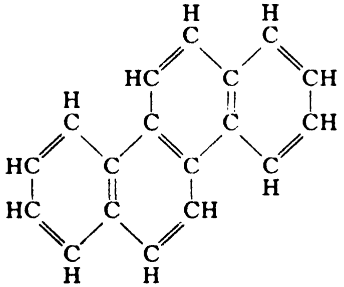
[200] E. Ginzburg, *Azer. Neft. Khoz.*, **1934** (9), 55; *Brit. Chem. Abs.* **B**, 1936, 676; *Chem. Abs.*, 1935, **29**, 6034.



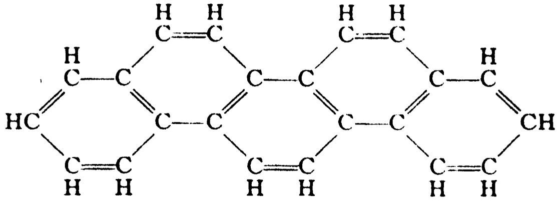
phenanthrene ($C_{14}H_{10}$)



anthracene ($C_{14}H_{10}$)



chrysene ($C_{18}H_{12}$)



picene ($C_{22}H_{14}$)

USES OF CRACKED PRODUCTS

Although the production of motor fuels from crude oils is the aim of cracking processes, this cannot be accomplished without the accompanying by-products, gas, tar and coke. The problem of utilization of these latter substances has formed the basis of an enormous synthetic industry of wide applications.[201]

Cracking gases rich in olefins may be converted into alcohols[202] and halides[203] or may be polymerized catalytically to form "polymer" gasoline.[204] Potolovskii and Anfinogenov[205] have used gases from vapor-phase cracking (containing 50 per cent ethylene) in place of acetylene for cutting and welding metals. Butkov and Rabinovich[206] determined the heating value of vapor-phase cracking gases to be 11,000-11,500 cals. per liter, and propose to use these gases as city gas, as others in the past have been. Gases rich in lower paraffins may be recracked at elevated temperatures in the presence of catalysts to form olefins which may subsequently be polymerized into liquid products.[207] This, however, is described in Chapters 2 and 26.

The liquid products also form a source of raw materials. Hall and Bachman[208] obtained 1-pentyne and 1-hexyne by brominating and dehalogenating[209] the corresponding olefins fractionated from a vapor-phase-cracked gasoline. Zilberman,

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[201] G. Egloff and J. C. Morrell, *Ind. Eng. Chem.*, 1934, **26**, 940; *Chem. Abs.*, 1934, **28**, 6988; *Brit. Chem. Abs.* **B**, 1934, 1044; *J. Inst. Pet. Tech.*, 1934, **20**, 527A. See also V. Pimenov, *Uspekhi Khim.*, 1933, **2**, 714; *Chem. Abs.*, 1934, **28**, 3570. Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., New York, 1934.

[202] See Chapters 11, 13, 14, 16, 17, 18.

[203] See Chapters 20 and 21.

[204] See Chapter 26.

[205] L. A. Potolovskii and P. Z. Anfinogenov, *Azer. Neft. Khoz.*, 1933, **8**, 96; *J. Inst. Pet. Tech.*, 1935, **21**, 143A; *Chem. Abs.*, 1934, **28**, 6691; *Brit. Chem. Abs.* **B**, 1935, 153.

[206] N. A. Butkov and E. I. Rabinovich, *Neft. Khoz.*, 1933, **25**, 88; *Brit. Chem. Abs.* **B**, 1934, 787; *Chem. Abs.*, 1934, **28**, 2503. See also H. G. Terzian, U. S. P. 1,963,811, June 19, 1934, to United Gas Improvement Co.; *Chem. Abs.*, 1934, **28**, 5218; *Brit. Chem. Abs.* **B**, 1935, 439.

[207] G. Egloff, U. S. P. 1,993,503, Mar. 5, 1935, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1936, 260; *J. Inst. Pet. Tech.*, 1935, **21**, 219A; *Chem. Abs.*, 1935, **29**, 2697. Also U. S. P. 1,972,926, Sept. 11, 1934; *Chem. Abs.*, 1934, **28**, 6995; *J. Inst. Pet. Tech.*, 1934, **20**, 581A. See also Chapters 2 and 26.

[208] H. J. Hall and G. B. Bachman, *Ind. Eng. Chem.*, 1936, **28**, 57; *Chem. Abs.*, 1936, **30**, 1356; *Brit. Chem. Abs.* **B**, 1936, 306.

[209] See Chapter 20 for a discussion of these methods.

Bolotin and Yakubovich[210] found that cracking residues reduce the oil adsorption capacity of pigments and believe that these residues may be substituted for linseed oil to the extent of 75 per cent in some coating compositions.

The tar obtained in cracking hydrocarbon oils at high temperatures and pressures contains resins which may be extracted from the residue by means of solvents, such as kerosene or naphtha.[211] These synthetic resins, being unsaponifiable, may be used for a variety of purposes. Frolich[212] suggests mixing about 1.5 per cent of petroleum resins with rubber compositions to improve the softening qualities and reduce the tendency of the rubber stock to adhere to the mill rolls. The addition of this type of resin has no effect on the curing time. Ellis[213] has proposed to incorporate these resins into paper ply and paperboard to provide greater strength and rigidity. Thus, the sheets of cardboard are coated with an emulsion of petroleum resin and water (formed by melting the resin and mixing with water and bentonite), pressed together, heated and calendered in a rolling machine to obtain uniform thickness. The resin emulsion may also be added to paper pulp as a sizing or an impregnating agent. The resins may be dissolved in gasoline and naphtha, mixed with a drying oil, and used as a paint.[214] The addition of wax is suggested for a waterproofing paint, the wax rendering the resins non-sticky but somewhat plastic when the paint is partially dry. Also, incorporation of a plasticizer such as benzene sulphonic acid increases the adhesion of the paint to metallic surfaces. Wood may be impregnated and stained with resins of such type[215] by heating them under pressure immersed in a solution of the resin in molten paraffin wax.

[210] G. Zilberman, A. Bolotin and S. Yakubovich, *Lakokrasochnuya Ind.*, **1933** (1), 37; *Brit. Chem. Abs.* B, 1933, 1042; *Chem. Abs.*, 1933, **27**, 4695.

[211] See Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[212] P. K. Frolich, U. S. P. 2,031,944, Feb. 25, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 2421.

[213] Carleton Ellis, U. S. P. 2,042,299, May 26, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 4954.

[214] P. K. Frolich, C. Winning and S. C. Fulton, U. S. P. 2,052,173, Aug. 25, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 7249.

[215] P. K. Frolich, U. S. P. 2,052,172, Aug. 25, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 6918.

Chapter 4

Production of Unsaturated Hydrocarbons by Pyrolysis

MONOLEFINS

Olefins are produced by thermal decomposition of various types of hydrocarbons and over a wide range of cracking conditions. The lower monolefins, which are important chemical intermediates, are obtained, for the most part, by the pyrolysis of paraffin hydrocarbons. Cycloparaffins also yield substantial proportions of olefins by thermal decomposition in the absence of catalysts but aromatics furnish only small proportions under the same conditions. Cracking of the lower paraffin hydrocarbons receives special attention in this chapter since they are available in large quantities and constitute the most promising raw materials.

In the pyrolysis of the lower paraffins, dehydrogenation to an olefin of the same number of carbon atoms is a relatively unimportant reaction except in the case of ethane and less so in the case of propane and isobutane. In general, decomposition of the molecule occurs mainly by rupture of the carbon bonds so that the olefins produced are lower in molecular weight than the parent paraffin.

The fundamental factors which influence the formation of olefins from aliphatic hydrocarbons are temperature, time of contact, pressure and nature of contact surface. Of these, temperature and time of contact are by far the more important and to some extent are mutually interchangeable. Thus, the results of cracking at low temperatures and long times of contact may be closely simulated by operating at somewhat higher temperatures and at shorter contact times. Since monolefins are usually primary decomposition products of paraffin hydrocarbons, contact time must be carefully controlled otherwise the olefins initially formed may be degraded or aromatized by too long heating periods. When a number of olefins are generated simultaneously by decomposition of a particular paraffin hydrocarbon, the evidence available indicates that the relative proportions at small conversions (i.e., short contact times) are but little influenced by temperature. However, with longer contact times the higher olefins tend to be partly converted into those of lower molecular weights so that ethylene ultimately becomes the main olefinic constituent of the reaction gas. In general, the optimum cracking temperature for olefin production from paraffin hydrocarbons varies considerably but 700°C. is a fair average temperature.

Often, temperatures used in the laboratory for pyrolysis observations are so much higher than those of industrial cracking that the discrepancy is noticeable. It should be remembered, however, that the implements of the laboratory far more easily permit the study of pyrolysis through a higher range of temperatures than sound commercial policy would indicate.

The influence of the pressure factor is not, however, perfectly clear. Since the primary decomposition reactions of paraffin hydrocarbons are homogeneous and first order, pressure should have little influence on the velocity of decomposition.

That this is approximately true has been demonstrated by a number of investigators. For example, the work of Munday[1] on the pyrolysis of *n*-pentane shows that the reaction velocity was approximately constant over a range of partial pressures of 0.1-1.0 atmospheres. Similar results have been obtained by Lang and Morgan[2] on the cracking of propane-steam mixtures at 700°C. On the other hand, however, it has been stated that reduction in pressure in the cracking of petroleum at 600-700°C. causes an increase in the rate of decomposition and a lowering in the temperature at which decomposition begins.[3] From the point of view of the production of olefins by pyrolysis the importance of the pressure factor probably resides mainly in its influence on the condensation and polymerization of the olefins initially formed. Such reactions are bimolecular and are thus favored by increase of pressure. Hence, it is advantageous to operate at low pressures, better sub-atmospheric, so as to minimize polymerization and condensation of the olefins produced. This is conveniently effected in vapor phase operations by employing an inert diluent gas, such as steam, thus reducing the partial pressure of the reacting hydrocarbon.

In the cracking of hydrocarbons (to olefins) it is usually best to avoid the use of heating surfaces, such as iron, nickel and some nickel alloys, which catalyze decomposition into carbon and hydrogen. Certain catalysts have been shown to accelerate dehydrogenation of paraffin to olefin hydrocarbons, but their applications appear to be limited because dehydrogenation is relatively unimportant except in a few cases, irreversible rupture of the carbon chain predominating in most instances. Gauzes of a copper-tin alloy, especially if treated with molybdic oxide, were found by Cambron[4] to aid the pyrolysis of ethane. Frey and Huppke[5] used a special chromic oxide gel in their investigation of the equilibria involved in the dehydrogenation of the lower paraffins. Boeckeler[6] studied various catalysts and ranked the materials tested in the following order of decreasing activity: copper gauze, zinc-copper on pumice, nickel gauze and stainless steel. However, none of these substances exhibited marked activity but merely lowered the temperature at which a given extent of reaction could be obtained without influencing the character of the reaction. Nickel, cobalt, copper or zinc, with or without promoters, have been recommended as contact agents for the pyrolysis of methane.[7] A reduced zinc oxide-chromium oxide catalyst has been suggested by Frolich and Boeckeler[8] for the production of olefins from paraffin hydrocarbons higher than methane. Passage of propane at 635°C. over this mixed oxide yielded a gas containing 14.3 per cent propene, 0.2 per cent ethylene, 26.1 per cent hydrogen and 59.4 per cent residual propane.

The work of Cambron and Bayley[9] indicates that when pyrolysis is carried out under conditions of turbulent flow the yields of olefins, at a given temperature, are greatly increased over those obtained with streamline flow. Furthermore, with turbulent flow higher rates of conversion of the lower paraffins to olefins are possible since the temperatures at which side reactions become important are considerably higher than when the gas flow is streamline. This influence of turbulent flow is associated with the more rapid transmission of heat from the tube walls to the body of the gas and to the elimination under such conditions of the stagnant superheated gas film on the tube wall which is so characteristic of streamline conditions. Rapid heat transmission is essential for olefin formation since all the reactions furnishing olefins from paraffin hydrocarbons are highly endothermic. The approximate heats of reaction of a number of these are as follows:

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[1] J. C. Munday, Dissertation, Columbia University, **1934**.

[2] J. W. Lang and J. J. Morgan, *Ind. Eng. Chem.*, 1935, **27**, 937; *Chem. Abs.*, 1935, **29**, 6204.

[3] N. Danaila and C. N. de Bie, *Bul. chim. soc. române chim.*, 1934, **37**, 37; *Brit. Chem. Abs.* **B**, 1935, 709; *Chem. Abs.*, 1935, **29**, 6740.

[4] A. Cambron, *Can. J. Research*, 1932, **7**, 646; *Chem. Abs.*, 1933, **27**, 1483.

[5] F. E. Frey and W. F. Huppke, *Ind. Eng. Chem.*, 1933, **25**, 54; *Brit. Chem. Abs.* **A**, 1933, 227; *Chem. Abs.*, 1933, **27**, 654.

[6] B. C. Boeckeler, M. S. Thesis, Mass. Inst. Tech., **1928**.

[7] H. Dreyfus, French P. 749,916, 1933; *Chem. Abs.*, 1934, **28**, 480.

[8] P. K. Frolich and B. C. Boeckeler, U. S. P. 1,944,419, Jan. 23, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1934, **28**, 2012; *Brit. Chem. Abs.* **B**, 1934, 917.

[9] A. Cambron and C. H. Bayley, *Can. J. Research*, 1933, **9**, 175; *Brit. Chem. Abs.* **B**, 1933, 949; *Chem. Abs.*, 1933, **27**, 5172. *Can. J. Research*, 1933, **9**, 583; *Chem. Abs.*, 1934, **28**, 1506; *Brit. Chem. Abs.* **B**, 1934, 308. U. S. P. 2,002,524 and 2,002,525, May 28, 1935; *Chem. Abs.*, 1935, **29**, 4373. British P. 425,606, 1935; *Brit. Chem. Abs.* **B**, 1935, 482; *Chem. Abs.*, 1935, **29**, 5549.

$$\begin{array}{lcll}
C_2H_6 & \rightarrow & C_2H_4 + H_2 & -\ 32{,}000 \text{ cal.} \\
C_3H_8 & \rightarrow & C_3H_6 + H_2 & -\ 32{,}000 \text{ cal.} \\
C_3H_8 & \rightarrow & C_2H_4 + CH_4 & -\ 16{,}100 \text{ cal.} \\
n\text{-}C_4H_{10} & \rightarrow & C_4H_8 + H_2 & -\ 32{,}000 \text{ cal.} \\
n\text{-}C_4H_{10} & \rightarrow & C_2H_4 + C_2H_6 & -\ 17{,}000 \text{ cal.} \\
n\text{-}C_4H_{10} & \rightarrow & C_3H_6 + CH_4 & -\ 17{,}600 \text{ cal.}
\end{array}$$

PRODUCTION OF OLEFINS FROM THE LOWER PARAFFIN HYDROCARBONS

As raw materials for the production of the lower olefins, which are of increasing importance in industrial synthesis, the lower paraffin hydrocarbons have obvious advantages since they are available in large quantities at a low price and their conversion to olefins can be readily accomplished with satisfactory yields.

The importance of turbulence has been demonstrated by the work of Cambron and Bayley,[10] who attained the necessary conditions by the use of silica tubes supplied with circular mica baffles spaced at distances of about 2 cm. apart. The effect of baffles in increasing the output of olefins in the pyrolysis of ethane, propane and *n*-butane is shown by the results obtained with a glazed quartz tube 2.0 cm. in diameter. (See Table 37.) The heated zone was 18.5 cm. in length.

TABLE 37.—*Pyrolysis in Empty and Baffled Quartz Tubes.*

(All Experiments at About 200 Liters/hr. Gas Rate)

Tube	Hydrocarbon	Temp. °C.	Expansion %	Analysis of Gaseous Products C_2H_2	C_2H_4	C_3H_6	C_4H_8	H_2	Olefins Produced g./hr.
Empty	Ethane	945°	35.8	0.8	27.6	—	0.4	29.2	99.4
"	Propane	950°	48.7	0.8	17.9	6.6	—	12.8	106.9
"	*n*-Butane	950°	63.0	0.9	15.8	10.5	2.7	10.7	152.1
Baffled	Ethane	950°	58.1	1.1	33.8	—	0.2	37.6	141.2
"	Propane	950°	73.5	0.9	23.1	11.9	—	16.1	182.4
"	*n*-Butane	922°	83.3	1.3	18.3	15.0	2.1	12.6	210.4

A systematic examination was made by Cambron and Bayley[11] of the effect of temperature and time of contact on the yield of olefins from ethane, propane and the butanes in baffled silica tubes. Their results indicate that, for a particular gas rate, the pyrolysis temperature for a given conversion to olefin could be materially reduced by increasing the length of the cracking zone. For example, the temperature required to convert 70 per cent of propane to olefins in a 20 cm. tube was 1087°C. but this was reduced to 960°C. in the case of a 40 cm. tube and to 885°C. by using a 80 cm. tube. This point is of practical significance since the latter temperature is not so severe as to exclude the possibility of using heat-resistant alloy steel tubes. These workers[12] have also reported on the pyrolysis of propane and *n*-butane in empty and baffled tubes constructed of certain heat-resistant alloys. Two alloys were investigated, one of the KA2S type containing about 18 per cent chromium and 8 per cent nickel, and another of a special alloy containing 28 per cent chromium and only traces of nickel. In both cases it was found advantageous to employ baffles to increase olefin production, and reduce the working temperature to the range of utility of special alloy steels. The KA2S alloy gave rise to considerable amounts of carbon, probably owing to the catalytic action of the nickel in the alloy. Tubes of the high-chromium alloy were, however, much better since only negligible carbon formation took place. It was noted, moreover, that the 28 per cent chromium alloy tube tended to deform slightly at 840°C. though no noticeable deformation occurred at 800°C. It was thought that any difficulty due to sagging could be eliminated by providing an adequate number of supports so as to decrease the unsupported length of tube in the furnace. It is reported,[13] nevertheless, that tubes of this alloy have been in successful use for over two years in vapor-phase cracking units operating at 870°C. Some results of Cambron and Bayley on the pyrolysis of propane in the chromium alloy tube (baffled) are given in Table 38.

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[10] A. Cambron and C. H. Bayley, *loc. cit.*

[11] A. Cambron and C. H. Bayley, *Can. J. Research*, 1933, 9, 175; *Brit. Chem. Abs.* B, 1933, 949; *Chem. Abs.*, 1933, 27, 5172.

[12] A. Cambron and C. H. Bayley, *Can. J. Research*, 1933, 9, 583; *Chem. Abs.*, 1934, 28, 1506; *Brit. Chem. Abs.* B, 1934, 308.

TABLE 38.—*Pyrolysis of Propane in Baffled 28% Chromium Alloy Tube.*

(Tubes of 2.54 cm. Bore)

Tube Length Cm.	Temp. °C.	Gas Rate l./hr.	Expansion %	Analysis of Gaseous Products % by Volume C_2H_2	C_2H_4	C_3H_6	H_2	Olefins Produced g./hr.	Yield % by Wt.
85	842°	393	79.3	0.6	25.1	14.1	17.5	408	53.2
140	800°	411	78.5	1.2	25.3	11.7	20.6	392	48.8
140	820°	517	80.1	1.3	27.2	10.7	10.7	508	50.4

Data on the production of ethylene and propene by pyrolysis of ethane and propane, respectively, at atmospheric pressure in helical KA2S tubes have been furnished by Sullivan, Ruthruff and Kuentzel.[14] The highest yield of ethylene was obtained from ethane at a temperature of 844°C. and at a contact time of 0.65 second. Under these conditions, conversion was 74 per cent and the exit gas contained 39 per cent of unsaturated hydrocarbons. In the case of propane, an 82 per cent conversion, calculated on a volume basis, into olefins (mainly ethylene) was secured at 820°C. with a contact time of one second. Because the major portion of the propane reacting formed ethylene and methane, the weight yield of olefins was appreciably lower than the volume yield. The influence of contact

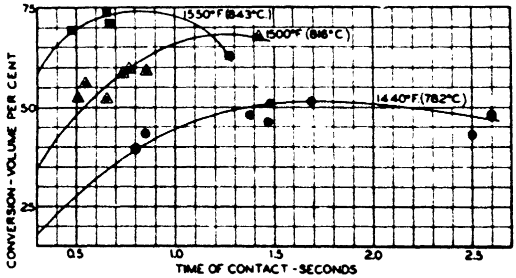

FIG. 47.
Influence of Contact Time on Thermal Conversion of Ethane to Olefins. (F. W. Sullivan, Jr., R. F. Ruthruff and W. E. Kuentzel)

Courtesy Industrial and Engineering Chemistry

time on the conversion of ethane and propane to olefin gases at various temperatures by pyrolysis in KA2S coils is shown in Figs. 47 and 48.

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[13] A. L. Foster, *Nat. Pet. News*, 1932, **24** (35), 27; *J. Inst. Pet. Tech.*, 1932, **18**, 471A. E. C. Wright, *Oil & Gas J.*, 1932, **31** (20), 57; *Chem. Abs.*, 1933, **27** 406. For a discussion of chromium alloy tubes used in cracking, see H. I. Newell, *Oil & Gas J.*, 1936, **34** (40), 32; *J. Inst. Pet. Tech.*, 1936, **22**, 208A; *Chem. Abs.*, 1936, **30**, 3213.

[14] F. W. Sullivan, R. F. Ruthruff and W. E. Kuentzel, *Ind. Eng. Chem.*, 1935, **27**, 1072; *J. Inst Pet. Tech.*, 1935, **21**, 408A; *Brit. Chem. Abs.* B, 1935, 979; *Chem. Abs.*, 1935, **29**, 7627.

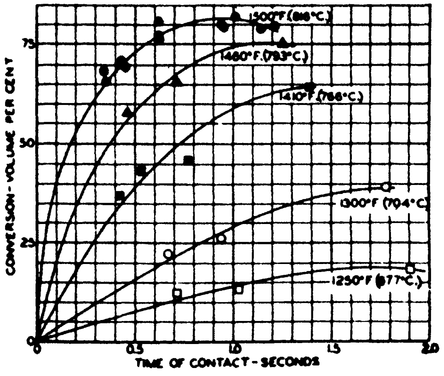

FIG. 48.
Effect of Contact Time in Propane Pyrolysis. (F. W. Sullivan, Jr., R. F. Ruthruff and W. E. Kuentzel)

Courtesy Industrial and Engineering Chemistry

The work of Frolich and Wiezevich[15] on the pyrolysis of propane and *n*-butane in silica reactors is of considerable interest in showing the effect of temperature on the olefin content of the exit gas, the contact time being maintained constant. The experimental results for propane are shown graphically in Fig. 49, from which it is seen that the olefin content (of the exit gas) is largest at about 880°C.

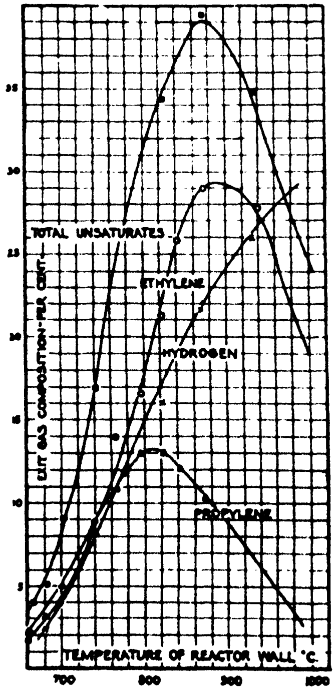

FIG. 49.
Olefin Content of Exit Gases from Propane Cracking at Various Temperatures. (P. K. Frolich and P. J. Wiezevich)

Courtesy Industrial and Engineering Chemistry

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[15] P. K. Frolich and P. J. Wiezevich, *Ind. Eng. Chem.*, 1935, 27, 1055; *J. Inst. Pet. Tech.*, 1935, 21, 408A; *Chem. Abs.*, 1935, 29, 7624; *Brit. Chem. Abs.* B, 1935, 980.

The maximum concentration of propene (13.2 per cent) occurred at a lower temperature, namely 810°C., than that, 890°C., required for the maximum concentration of ethylene (29.4 per cent). In the case of *n*-butane (Fig. 50) the greatest total olefin content of the reaction gas was obtained at 690°C. The temperature at which the propene concentration is at a maximum (11.1 per cent at 650°C.) is somewhat lower than that (730°C.) for maximum ethylene content, namely 29 per cent. The highest concentration of butene, 8.1 per cent, was secured at about 670°C.

Interesting results have been reported by Frolich and Wiezevich on cracking propane in a copper tube in the presence of about 70 per cent of air in the inlet gas. Under these conditions 75-80 per cent of the propane was converted into unsaturated hydrocarbons at 675° ± 15°C. and a contact time of about 30 seconds. The unsaturated hydrocarbons formed consist of ethylene and propene in the ratio of 3 parts of ethylene to 2 of propene. The conversions obtained in the presence of air may be compared with the optimum conversion of 60-70 per cent by straight cracking at 700°C. using a copper-coated steel reactor. When air was admixed with propane, Frolich and Wiezevich noted that the material constituting the reactor exerted some influence on the course of reaction. At temperatures below 560°C. a mild steel reactor gave higher yields of unsaturated hydrocarbons than one of copper. At 600°C. and above, copper was much more satisfactory since at these temperatures iron apparently catalyzed polymerization of the olefins into liquid and solid tars. In the presence of air, glass seems to exert a slight inhibiting action on the cracking.

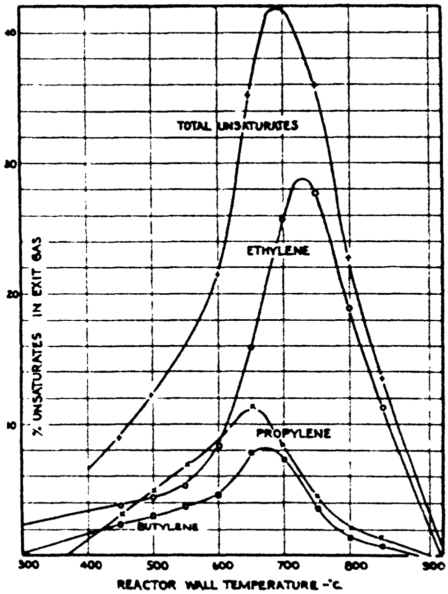

FIG. 50.
Effect of Temperature on Olefin Production in Pyrolysis of *n*-Butane. (P. K. Frolich and P. J. Wiezevich)

Courtesy Industrial and Engineering Chemistry

PRODUCTION OF LOWER OLEFINS FROM HIGHER HYDROCARBONS

The production of the lower olefins by pyrolysis of pentanes, hexanes and heptane in baffled quartz tubes at temperatures of about 1000°C. has been inves-

tigated by Cambron and Bayley.[16] Typical results obtained by these investigators using a silica tube (20 cm. long and 2.7 cm. internal diameter) with mica baffles are given in the appended Table 39.

TABLE 39.—*Pyrolysis of Paraffin Hydrocarbons in Baffled Silica Tube.*

Hydrocarbon	Temp. °C.	Liquid Feed g./hr.	Analysis of Gaseous Products, % by Vol. C_2H_4	C_3H_6	C_4H_8	H_2	Olefins Produced g./hr.
n-Pentane	1071	1080	26.7	20.3	1.5	12.1	475
"	1075	1158	24.0	20.3	1.1	9.5	475
"	1070	1404	24.3	17.6	—	8.9	392
Isopentane	1075	1080	19.4	18.9	4.5	11.3	474
"	1072	1105	20.7	19.9	3.5	11.1	465
Mixed Hexanes	952	905	29.0	19.7	2.1	12.3	544
"	1032	910	27.1	23.1	3.3	10.4	480
"	1081	872	30.0	21.6	—	11.5	442
Commercial Heptane	1043	1060	27.6	24.2	2.9	10.8	426
	1075	1042	29.0	24.5	1.5	11.4	483
	1093	767	31.6	12.5	0.6	16.8	384

It is evident that pyrolysis of the lower liquid paraffins can be controlled to yield gaseous products containing 50-55 per cent by volume of olefins consisting of approximately equal amounts of ethylene and propene. The experiments summarized above were all characterized by the absence of tar formation and carbon deposition in spite of the high temperatures employed and the high concentration of olefins in the gaseous products.

Matignon and Seon[17] report that water vapor exerts a marked influence on the yield of ethylene (and its homologues) from heptane.[17a] For example, these investigators observed that in the absence of water and at 700°C. the paraffin gave 39 per cent of ethylene. On the other hand when the ratio of heptane to water vapor was 2:7 (by weight) and the temperature 800°C., 50 per cent of ethylene was obtained. Increasing the proportion of water to paraffin (5:2) and the temperature (to 935°C.) raised the yield to 76 per cent of ethylene.

Danaila and de Bie[18] investigated the production of ethylene by vapor-phase cracking, at 600-720°C. under an absolute pressure of 150 mm., of a light kerosene fraction. Under these conditions 70-95 per cent of the oil was converted into gas containing substantial proportions of ethylene while no low boiling liquids were formed. At 740-750°C. carbon formation is less than 3-4 per cent of the oil used. Reduction of pressure was found to lower the initial decomposition temperature of the oil and to increase the proportion of ethylene in the gas. If aromatic hydrocarbons are removed from the oil prior to pyrolysis, a gas containing 45 per cent of ethylene can be obtained, representing 47 per cent of the oil employed. Separation of the higher olefins from this gas raises the ethylene content to over 55 per cent by volume.

In the cracking of gasoline and kerosene fractions (from the same crude oil) in a quartz tube, optimum olefin production, according to Candea and Kühn,[19] occurred at temperatures of 700°C. and 600°C., respectively. High olefin yields were favored by short heating periods.

The decomposition of the higher boiling fractions (Kogasin II) of the paraffinic benzine obtained from hydrogen and carbon monoxide by the Fischer-Tropsch process,[20] has been studied by Pichler.[21] The reaction, carried out in narrow tubes to enhance the ratio of heating surface to reaction volume and to avoid overheating of the walls, furnished up to 75 per cent of gaseous olefins together with volatile, liquid, aromatic and unsaturated hydrocarbons, the remaining 25 per cent consisting of saturated gaseous hydrocarbons, undecomposed paraffin oil and aromatic tar. Above 600°C., gaseous olefins predominated in the products, the yields rising from 20 per cent by weight at 550°C. and 0.4 second contact time to 62 per cent at 700°C. and 0.14 second. Similar results were secured by pyrolysis of Kogasin II with an electrically heated platinum wire. Under the latter conditions, the products consisted of 20 per cent of highly unsaturated liquid and 80 per cent of gaseous hydrocarbons. Of the latter, 70 per cent (by volume) were unsaturated and consisted principally of ethylene or its homologues.[22] Use of an electrically heated graphite rod in place of the platinum wire gave 14.7 per cent liquid and 85.3 per cent gaseous products.[22a] The latter contained 12.7 per cent hydrogen, 69 per cent unsaturated and 18.3 per cent saturated hydrocarbons.

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[16] A. Cambron and C. H. Bayley, *Can. J. Research*, 1933, **9**, 175; *Chem. Abs.*, 1933, **27**, 5172; *Brit. Chem. Abs.* **B**, 1933, 949.

[17] C. Matignon and M. Seon, *Compt. rend.*, 1934, **198**, 1649; *Brit. Chem. Abs.* **A**, 1934, 752.

[17a] *Cf.* Aquolization discussed in Chapter 3.

[18] N. Danaila and C. N. de Bie, *Bul. chim. soc. române chim.*, 1934, **37**, 37; *Brit. Chem. Abs.* **B**, 1935, 709; *Chem. Abs.*, 1935, **29**, 6740.

[19] C. Candea and J. Kühn, *Bull. sci. ecole polytech. Timisoara*, 1934, **5**, 97; *Chem. Abs.*, 1935, **29**, 8304; *J. Inst. Pet. Tech.*, 1935, **21**, 125A.

Candea and Manughevici[23] studied the thermal decomposition of a Rumanian kerosene fraction both in the presence and absence of catalyst. Best yields of ethylene were obtained at 800°C. and the use of copper surfaces, either in the form of tubes or shavings in glass reactors, was found to impede carbon formation.

It is interesting to note that ethylene may be prepared from peat or cracked tar at 600-700°C. by air-blowing.[24] Aluminum and ferric oxides apparently have no catalytic effect on the reaction. In some instances alcohols may serve as the source of olefins. For example, Sakmin[25] made ethylene by passing ethyl alcohol over unglazed porcelain in a copper tube at 400-500°C. At lower temperatures (300°C.) propene was obtained. Triebs[26] observed that amorphous clay exerted a greater catalytic effect than porcelain. If a pressure autoclave is used, a temperature of 200-350°C. is necessary. Ipatieff[27] points out that pure copper is not a catalyst for the decomposition of alcohols, and he recommends alumina.

HIGHER OLEFINS BY PYROLYSIS

The production of higher olefins, for example, pentene, hexene and higher, is intimately associated with the cracking industry. Gasolines from commercial cracking processes, especially from so-called vapor-phase operations at 500-600°C., are relatively rich in olefin hydrocarbons. A discussion of the various types of unsaturated hydrocarbons found in such gasolines is given in Chapter 3, from which it will be seen that the available information is still incomplete.

It is interesting to note that both indene and styrene, two aromatic monolefin hydrocarbons of value in the manufacture of synthetic resins, have been isolated from the products of pyrolysis of Persian natural gas at temperatures of about 850°C. Using a gas rich in propane and butane, the yields of styrene and indene are about 2.4 and 0.95 liters, respectively, per 100 cubic meters of gas pyrolyzed. Birch and Hague[28] consider that the most probable mechanism of the formation of styrene is by direct combination of ethylene and benzene to furnish ethylbenzene, which can then dehydrogenate to styrene.

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[20] For discussion of this method of preparing hydrocarbons, see Chapter 52.

[21] H. Pichler, *Brennstoff-Chem.*, 1935, 16, 404; *J. Inst. Pet. Tech.*, 1936, 22, 45A; *Chem. Abs.*, 1936, 30, 3980.

[22] F. Fischer, K. Peters and K. Winzer, *Brennstoff-Chem.*, 1935, 16, 421; *Brit. Chem. Abs.* B, 1936, 133; *Chem. Abs.*, 1936, 30, 3991; *J. Inst. Pet. Tech.*, 1936, 22, 141A.

[22a] K. Peters and K. Winzer, *Brennstoff-Chem.*, 1936, 17, 429; *Chem. Abs.*, 1937, 31, 1990; *Brit. Chem. Abs.* B, 1937, 107.

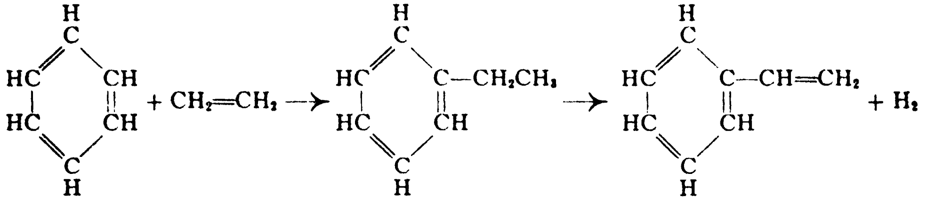
[23] C. Candea and C. Manughevici, *Bull. sci. école polytech. Timisoara*, 1936, 6, 298; *Chem. Abs.*, 1936, 30, 7318.

[24] B. P. Federov and P. A. Semenov, *Khim. Tverdogo Topliva*, 1932, 3, 743; *Brit. Chem. Abs.* B, 1935, 6; *Chem. Abs.*, 1934, 28, 5964.

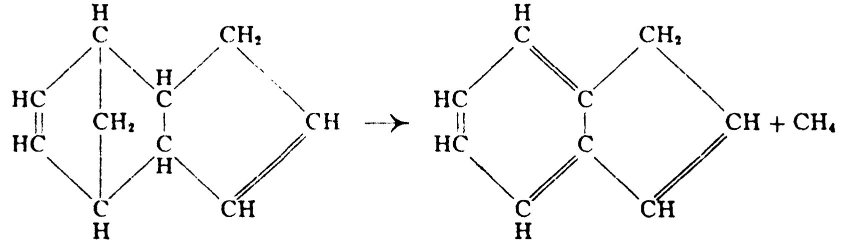
[25] P. K. Sakmin, *Ber.*, 1934, 67, 392; *Brit. Chem. Abs.* A, 1934, 508; *Chem. Abs.*, 1934, 28, 3049.

[26] W. Triebs, *Ber.*, 1934, 67, 942; *Chem. Abs.*, 1934, 28, 5037; *Brit. Chem. Abs.* A, 1934, 864.

[27] V. N. Ipatieff, *Ber.*, 1934, 67, 1061; *Chem. Abs.*, 1934, 28, 5037; *Brit. Chem. Abs.* A, 1934, 864.



It is not so easy to account for the indene, which might be formed (1) by reaction between propene and benzene to give propylbenzene, convertible into indene by ring closure and dehydrogenation; (2) by a somewhat similar reaction between toluene and ethylene involving the formation of ethyltoluene or propylbenzene followed by ring closure and dehydrogenation or (3) by demethanation of dicyclopentadiene as follows:



The suggested mechanism for the formation of styrene was confirmed by pyrolysis of an equimolecular mixture of ethylene and benzene at 820°C., the products containing 40 per cent of styrene in the fraction boiling higher than benzene. No experimental evidence could be obtained in support of any of the suggested reactions for the formation of indene.

TECHNICAL PROCESSES FOR OLEFIN PRODUCTION

The influence of pressure on the production of olefins by pyrolysis of saturated hydrocarbons has already been discussed and it has been shown low partial pressures are favorable since polymerization and condensation reactions are thereby largely suppressed. High temperature pyrolysis at pressures below atmospheric is hardly practicable on an industrial scale so that a diluent is usually employed to reduce the partial pressure of the reacting hydrocarbon vapors. Steam is often used for this purpose but the oxides of carbon, e.g., 5-20 per cent of carbon dioxide, are suggested by Dreyfus.[29] Instead of subjecting the mixture of hydrocarbon vapor and inert diluent gas to heat treatment, the latter may be preheated to a sufficiently high temperature so that on incorporating with the hydrocarbon vapor the resulting blend is at a temperature high enough to effect pyrolysis.[30] Thus, Grebe, Coleman and Reilly[31] produce gaseous olefins by adding oil vapors to sufficient steam, superheated to 950-1200°C., so that the resulting mixture attains a temperature of about 800-1000°C. An electrical heating coil, shown in Fig. 51, may be employed for increasing the temperature of the steam. The reactants are then passed over magnetic iron oxide.

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[28] S. F. Birch and E. N. Hague. *Ind. Eng. Chem.*, 1934, **26**, 1008; *J. Inst. Pet. Tech.*, 1934, **20**, 523A; *Brit. Chem. Abs.* **B**, 1934, 1049; *Chem. Abs.*, 1934, **28**, 6982.

[29] H. Dreyfus. French P. 750.496, 1933; *Chem. Abs.*, 1934, **28**, 776.

[30] H. Dreyfus. French P. 763.942, 1934; *Chem. Abs.*, 1934, **28**, 5467.

[31] J. J. Grebe, G. H. Coleman and J. H. Reilly, U. S. P. 1,962,502, June 12, 1934, to Dow Chemical Co.: *Chem. Abs.*, 1934, **28**, 4896; *Brit. Chem. Abs.* **B**, 1935, 343.

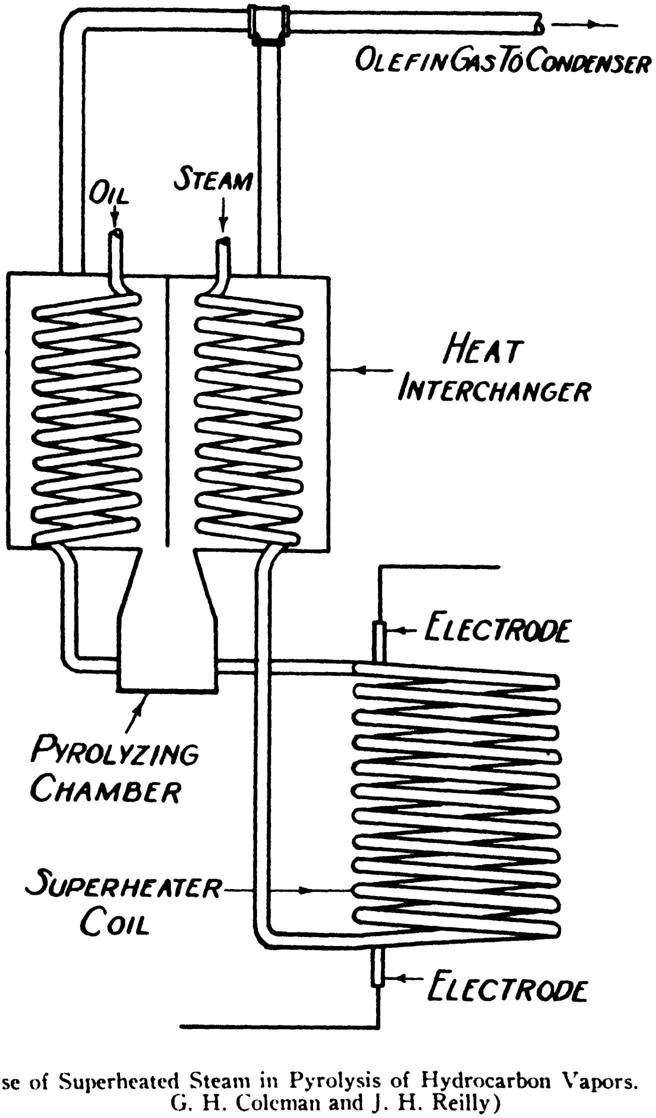

FIG. 51.—Use of Superheated Steam in Pyrolysis of Hydrocarbon Vapors. (J. J. Grebe, G. H. Coleman and J. H. Reilly)

An apparatus for cracking hydrocarbon vapors at 600-1200°C. and 0.005 to 0.1 second contact time is described by Tropsch.[32] It consists of a vertical annular vessel, placed in a down-draft furnace, and heated by flames impinging on the inside and outside near the lower end through which the hydrocarbons are admitted to the reaction zone.

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[32] H. Tropsch, U. S. P. 1,981,129, Nov. 20, 1934, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1935, 882; *Chem. Abs.*, 1935, **29**, 474. *Cf.* U. S. P. 2,045,255, June 23, 1936; *Chem. Abs.*, 1936, **30**, 5597.

Instead of using an externally heated tube, it has been proposed[33] to employ a converter filled with refractory material which is first raised to a sufficiently high temperature by downward passage of hot gaseous products of combustion. After removal of the latter by a current of steam or gas, pyrolysis of gaseous hydrocarbons is effected by passage of these in an upward direction over the refractory material. The cycle is then repeated. When natural gas is the raw material, a portion of this may be burned thus heating the reaction zone to 800°C.[34] During combustion untreated gas is introduced, and the resulting product is a mixture having a B.t.u. value of about 800.

Dreyfus[35] produces unsaturated hydrocarbons from paraffins (boiling below 150°C.) by conducting their vapors through organic liquids or semi-liquids (containing suspended carbon) at temperatures of 300-350°C. For example, a gas consisting of ethane and propane is pyrolyzed by passage, under 5 atmospheres pressure, through a cracking residuum at 450°C.

A number of catalysts have been described for the preparation of olefins from paraffins (usually by dehydrogenation), examples of such being sulphur, arsenic, antimony, selenium or tellurium.[36] Other contact agents include zinc chloride[37] and coke.[38] A small proportion of a halogen, such as iodine, is said to accelerate formation of olefins from propane at 575-650°C.[39] Catalysts consisting of the halides of copper, silver, zinc, cadmium, thallium, tin, lead, titanium, silicon, vanadium, bismuth, molybdenum, tungsten, uranium, manganese, rhenium, nickel, iron and cobalt or of the elements selenium, tellurium, arsenic, antimony, or carbon are reported[40] to effect dehydrogenation of normally liquid saturated hydrocarbons at temperatures of 200-500°C. In some instances, hydrogen chloride or chlorine may be admixed with the hydrocarbon vapors, and the latter conducted over metals (e.g., manganese or zinc) at 400-500°C.[41] Difficulty reducible oxides or sulphides, such as tungstic oxide on carbon, may be employed with solid paraffin hydrocarbons at 400° to 500°C. and atmospheric or reduced pressures.[42] Dreyfus[43] prepares ethylene (and also ethane) by conducting methane over a catalyst (nickel, cobalt, copper or zinc) at 350-850°C. Pyrolysis of gaseous hydrocarbons at 400-1100°C. in the presence of 2 per cent of mercury[44] or 0.01 per cent of cadmium[45] vapor has been suggested. Also, it has been pointed out that the oxides of bi- and trivalent chromium may be employed.[46] It is reported[47] that dehydrogenation of higher paraffin hydrocarbons, without substantial rupture of carbon bonds, can be effected at 800-900°F. and at about atmospheric pressure in the presence of catalysts such as alumina, thoria, and the oxides or sulphides of the metals of Group 6 of the Periodic Table.

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[33] F. M. Pyzel, U. S. P. 1,983,992, Dec. 11, 1934, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 914. British P. 392,643, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1933, **27**, 5529; *Brit. Chem. Abs.* **B**, 1933, 614.

[34] J. B. Garner, R. W. Miller and G. B. Seyden, U. S. P. 1,954,991, Apr. 17, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1934, **28**, 3875; *Brit. Chem. Abs.* **B**, 1935, 214.

[35] H. Dreyfus, British P. 401,286, 1933; *Chem. Abs.*, 1934, **28**, 2515; *Brit. Chem. Abs.* **B**, 1934, 136.

[36] A. J. van Peski, German P. 605,737, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1935, **29**, 1832; *J. Inst. Pet. Tech.*, 1935, **21**, 99A

[37] A. D. Petrov, *Neft. Khoz.*, 1932, **22**, 95; *Brit. Chem. Abs.* **B**, 1932, 969; *Chem. Abs.*, 1932, **26**, 4455.

[38] P. Feiler and H. Haeuber, U. S. P. 2,007,754, July 9, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 5855; *J. Inst. Pet. Tech.*, 1935, **21**, 381A.

[39] A. J. van Peski, U. S. P. 1,925,421, Sept. 5, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1933, **27**, 5337.

[40] British P. 409,312, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5830; *J. Inst. Pet. Tech.*, 1934, **20**, 425A; *Brit. Chem. Abs.* **B**, 1934, 665. For the cracking of amines containing more than 8 carbon atoms and the employment of metallic chlorides or acids (e.g., phosphoric acid) as catalysts, see British P. 436,345, 1935, to H. T. Böhme A.-G.; *Brit. Chem. Abs.* **B**, 1936, 54.

[41] British P. 442,592, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1936, 357; *Chem. Abs.*, 1936, **30**, 5022.

[42] C. Wulff, German P. 596,094, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 4430.

[43] H. Dreyfus, British P. 399,526, 1932; *Brit. Chem. Abs.* **B**, 1933, 1046; *Chem. Abs.*, 1934, **28**, 1713.

[44] F. Winkler and H. Haeuber, U. S. P. 1,986,238, Jan. 1, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1098; *J. Inst. Pet. Tech.*, 1936, **22**, 53A; German P. 626,338, 1936; *Chem. Abs.*, 1936, **30**, 3439.

The cracking of ethylbenzene to styrene may be accomplished at about 500-700°C. in the presence of ceria or zinc and an oxide of tungsten, uranium or molybdenum.[48]

The development of construction materials for tubes used in the pyrolysis of saturated hydrocarbons has been the subject of much investigation. Not only must the tubes be capable of withstanding the necessary high temperatures for prolonged periods of time but they must not catalyze carbon formation and should accelerate the olefin-forming reactions. Special heat-resisting alloys or refractory silicious materials have been employed for this purpose but the latter suffer from the disadvantage of low mechanical strength, thus necessitating the use of comparatively thick-walled retorts with consequent poor heat transfer. In the large scale pyrolysis of Persian natural gas, a special alloy steel (H.R.4) containing 26 per cent of chromium and not more than 0.3 per cent nickel was found most applicable.[49] Prolonged contact of this alloy at temperatures of about 1000°C. resulted in some embrittlement, which may be suppressed by an increase in the nickel content. Reference has already been made to the tests carried out by Cambron and Bayley using high-chromium steels.

Pyrolysis of saturated hydrocarbons, diluted with steam, may be effected at 600-900°C. in reactors consisting of a chromium steel containing less than 2 per cent of nickel or of iron of low nickel content and externally coated with a layer of heat-resisting chromium-nickel steel.[50] Alloys containing 50-80 per cent of nickel, 10-25 per cent of chromium and 4 to 30 per cent of iron have been used at temperatures of 700-1000°C.[51] Externally-heated silicon tubes are reported to show a decided promise in suppressing carbon formation under properly controlled conditions.[52] Parts of apparatus exposed to temperatures above 500°C. may be composed of or lined with a composition containing free silicon which has been molded into tubes (or other shapes) by the usual ceramic processes.[53] Alternatively, internal coatings of a high-melting element, especially silicon or titanium, may be secured by firing the latter in powder form in the apparatus.[54] In some instances, tubes of silicon, or a metal silicide, are encased in steel tubes, a layer of alumina cement being interposed to prevent the formation of an alloy between the silicon and the outer steel casing.[55] For temperatures above 500°C., it has been proposed to use glazes of the silicates, phosphates and borates of copper, manganese, lead or chromium applied internally on supports of refractory material such as the silicides, carbides or chamotte.[56] Internal linings of tin, lead, molybdenum, chromium or tungsten are obtained by decomposition within the apparatus of certain compounds of the metal. Metallic alkyls, carbonyls or volatile chlorides may be employed for this purpose.[57] Winkler and Haeuber[58] propose the use of internally tinned manganese-copper tubes for the production of the lower olefins from gaseous paraffins at about 700°C. In one process it has been recommended that the cracking tube be employed in a vertical position.[59] At the upper end of the latter is placed a reflux condenser which returns unreacted substances to the cracking zone. In this manner the conversion of a coal-oil distillate to olefins is said to be effected.

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[45] F. Winkler and H. Haeuber, U. S. P. 1,986,239, Jan. 1, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1099; *J. Inst. Pet. Tech.*, 1936, **22**, 53A.

[46] French P. 795,825, 1936, to Usines de Melle. (Soc. anon.); *Chem. Abs.*, 1936, **30**, 5588.

[47] British P. 434,311, 1935, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1935, 1034; *Chem. Abs.*, 1936, **30**, 849.

[48] G. D. Graves, U. S. P. 2,036,410, April 7, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 3446.

[49] W. H. Cadman, *Ind. Eng. Chem.*, 1934, **26**, 315; *Chem. Abs.*, 1934, **28**, 2499; *Brit. Chem. Abs.* **B**, 1934, 486.

[50] British P. 404,984, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1934, 310; *Chem. Abs.*, 1934, **28**, 4429.

[51] C. J. Strosacker and H. S. Kendall, U. S. P. 1,983,415, Dec. 4, 1934, to Dow Chemical Co.; *Chem. Abs.*, 1935, **29**, 593; *Brit. Chem. Abs.* **B**, 1935, 1126.

[52] F. Winkler, H. Haeuber and P. Feiler, U. S. P. 1,922,918, Aug. 15, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, **27**, 5082. U. S. P. 1,937,619, Dec. 5, 1933; *Chem. Abs.*, 1934, **28**, 1182.

[53] F. Winkler, H. Haeuber and P. Feiler, German P. 593,257, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 3078. F. Winkler and H. Haeuber, German P. 602,444, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 473.

[54] F. Winkler and H. Haeuber, German P. 590,875, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 3078.

[55] F. Winkler, H. Haeuber and P. Feiler, German P. 602,443, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 473. *Cf.* French P. 799,224, 1936; *Chem. Abs.*, 1936, **30**, 7582.

Pyrolysis of hydrocarbons at atmospheric pressure in the presence of oxygen or oxygen-containing gases is of interest since part of the heat required is supplied by incomplete combustion. The results of Frolich and Wiezevich[60] with propane-air mixtures have already been discussed. The conversion of saturated gaseous hydrocarbons to unsaturated hydrocarbons by heating to 570-1200°C. under practically normal pressure and in the presence of a small proportion of a gas containing free oxygen has been described.[61]

In general, olefins having less than ten carbon atoms may be converted into those of higher molecular weights by heat treatment[62] at 550-650°C. in the presence of not more than 5 per cent oxygen. Herrmann and Baum[63] prepared acetylene by conducting ethylene, with insufficient oxygen for complete combustion, over catalysts at temperatures up to 1000°C. and at space velocities of about 160 liters per liter of reaction space.

Olefin hydrocarbons, containing at least 5 carbon atoms, may be obtained by the vapor-phase cracking of mixtures composed essentially of aliphatic hydrocarbons, for example, paraffin wax or mixtures containing more than 20 per cent of paraffin wax, and submitting the products to fractionation.[64]

In two-stage processes for the conversion of paraffin hydrocarbon gases into liquid hydrocarbons by intermediate formation of olefins and subsequent polymerization of same, it is often proposed to conduct the first stage under pressure. Thus, Wagner[65] pyrolyzes natural gas at 1250-1350°F. under a pressure of 30 lb. per sq. in., the gaseous olefinic portion of the product being removed and polymerized at higher pressures and lower temperatures. In making liquid hydrocarbons from butane and propane, Frey[66] recommends the intermediate formation of olefins be carried out above 540°C. and under a pressure of 1000-5000 lb. per sq. in., and subsequent polymerization be effected at lower temperatures and the same pressure. In another procedure, Coxon[67] passes a stream of natural gas of restricted cross sectional area into a stream of inert gas previously heated above the reaction temperature. The gases unite in a reaction chamber and condensable liquid material is separated as it leaves the heated zone.

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[56] F. Winkler, P. Feiler and H. Weigmann. U. S. P. 1,987,092, Jan. 8, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1430; *J. Inst. Pet. Tech.*, 1935, **21**, 137A.

[57] P. Feiler, German P. 590,874, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 3078. French P. 750.869, 1933; *Chem. Abs.*, 1934, **28**, 1046.

[58] F. Winkler and H. Haeuber, U. S. P. 1,945,960, Feb. 6, 1934; *Chem. Abs.*, 1934, **28**, 2363.

[59] H. P. Stephenson and R. G. Israel, British P. 451,575, 1936; *Brit. Chem. Abs.* **B**, 1936, 969; *J. Inst. Pet. Tech.*, 1936, **22**, 439A.

[60] P. K. Frolich and P. J. Wiezevich, *Ind. Eng. Chem.*, 1935, **27**, 1055; *Brit. Chem. Abs.* **B**, 1935, 980; *Chem. Abs.*, 1935, **29**, 7624; *J. Inst. Pet. Tech.*, 1935, **21**, 408A.

[61] French P. 754.000, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1046. *Cf.* British P. 447.470, 1936; *Chem. Abs.*, 1936, **30**, 6761. Also French P. 792,101, 1935; *Chem. Abs.*, 1936, **30**, 4175.

[62] British P. 432,430, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 893; *Chem. Abs.*, 1936, **30**, 484.

[63] W. O. Herrmann and E. Baum, U. S. P. 1,898.301, Feb. 21, 1933, to Consortium für elektrochemische Industrie; *Brit. Chem. Abs.* **B**, 1933, 954; *Chem. Abs.*, 1933, **27**, 2691.

[64] French P. 773.231, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1935, **29**, 1617. British P. 426,843, 1935; *Brit. Chem. Abs.* **B**, 1935, 539; *Chem. Abs.*, 1935, **29**, 6418. *Cf.* British P. 443.263, 1936; *Brit. Chem. Abs.* **B**, 1936, 536; *Chem. Abs.*, 1936, **30**, 4873.

[65] C. R. Wagner, U. S. P. 1,976.591, Oct. 9, 1934, to Pure Oil Co.; *J. Inst. Pet. Tech.*, 1935, **21**, 26A; *Chem. Abs.*, 1934, **28**, 7486.

[66] F. E. Frey, U. S. P. 1,987.007, Jan. 8, 1935, to Phillips Petroleum Co.; *Chem. Abs.*, 1935, **29**, 1619; *J. Inst. Pet. Tech.*, 1935, **21**, 137A.

Separation of Lower Olefins from Gas Mixtures

Separation of the lower olefin hydrocarbons from gas mixtures containing (in addition to olefins) hydrogen, paraffin hydrocarbons, butadiene, and, in some cases, acetylene is an important technical problem since relatively pure olefins must be employed in certain industrial syntheses. Both chemical and physical methods, including absorption and adsorption, have been suggested for this purpose. A typical chemical mode of segregation may be employed for the production of alcohols from olefins by absorption in sulphuric acid in several stages, each successive stage representing sulphating conditions more or less specific for one particular olefin. Thus, propene and ethylene may be extracted from gaseous mixtures by absorbing the former olefin in 80-90 per cent sulphuric acid at 20-23°C. and 10-25 atmospheres pressure and subsequently absorbing the latter hydrocarbon in sulphuric acid of 75-85 per cent strength at 90-130°C. and 10-25 atmospheres pressure.[68] According to Engs and Moravec,[69] olefins of the type $RCH{=}CHR$ and $R_2C{=}CHR$ may be removed from hydrocarbon mixtures by treatment with 60-70 per cent aqueous sulphuric acid at 0-25°C., whereby they are selectively converted into their sulphuric mono esters. On heating the acid liquor, these mono alkyl sulphates are transformed into polymers of the original olefins. Ethylene or concentrates rich in ethylene are prepared by Markovich and Pigulevskii[70] by first eliminating higher hydrocarbons with sulphuric acid and then treating with organic solvents, compressing, cooling and rectifying under pressure.

Separation of olefins from hydrocarbon gas mixtures by liquefaction under pressure followed by pressure fractionation has been developed by a number of industrial concerns, including The Air Reduction Co. in U.S.A. and the Linde Air Products Co. in Germany. When the olefins and paraffins possess the same number of carbon atoms this procedure is somewhat difficult because of the closeness of physical constants (e.g., vapor pressures) of the hydrocarbons. The physical characteristics of ethane and ethylene, however, are sufficiently divergent to render separation easily possible. A continuous process for the segregation of ethylene from complex gas mixtures has been described by Van Nuys[71] in which the mixture is subjected to selective liquefaction, followed by rectification of the liquid portions. Carney[72] recommends a two-stage fractionating system for the separation of a particular liquid olefin from cracked oils. In the first stage, concentration of the desired product into one fraction is effected by distillation. The latter is subjected to a second rectification to give further segregation of the compound, the residue being returned to the first stage. It is reported by Deanesly[73] that pressure fractionation of liquid olefins from liquid paraffins is facilitated by the presence of liquid ammonia. The latter is said to have a greater affinity for olefins than for paraffins. In the procedure, a mixture of olefins and paraffins is fractionally distilled in the presence of anhydrous liquid ammonia. The distillate is condensed, cooled and led to a separator (Fig. 52). In the latter the ammonia and olefins are drawn off from the lower layer and returned to the still, and the paraffins are removed from the upper portion of the separated distillate. Another example of this procedure is the successive condensation of propene and ethylene followed by fractionation of the individual

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[67] G. H. Coxon, U. S. P. 1,971,667, Aug. 28, 1934, to Gasoline Products Co.; *Chem. Abs.*, 1934, **28**, 6553; *J. Inst. Pet. Tech.*, 1934, **20**, 535A.

[68] W. H. Groombridge, British P. 415,766, 1934, to British Celanese Ltd.; *Chem. Abs.*, 1935, **29**, 811; *Brit. Chem. Abs.* **B**, 1934, 952. Also H. Dreyfus and W. H. Groombridge, British P. 403,654, 1933, to British Celanese Ltd.; *J. Inst. Pet. Tech.*, 1934, **20**, 336A; *Brit. Chem. Abs.* **B**, 1934, 355; *Chem. Abs.*, 1934, **28**, 3415.

[69] W. Engs and R. Moravec, U. S. P. 2,007,159, July 9, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 5456; *J. Inst. Pet. Tech.*, 1936, **22**, 53A; *Brit. Chem. Abs.* **B**, 1936, 632. Canadian P. 338,207, 1933; *Chem. Abs.*, 1934, **28**, 1713. *Cf.* French P. 795,399, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 5241.

[70] M. B. Markovich and V. V. Pigulevskii, Russian P. 29,165 and 29,171, 1933; *J. Inst. Pet. Tech.*, 1934, **20**, 458A; *Chem. Abs.*, 1933, **27**, 3951, 4069.

[71] C. C. Van Nuys, U. S. P. 1,958,553 and 1,958,554, May 15, 1934, to Air Reduction Co.; *Chem. Abs.*, 1934, **28**, 4436; *Brit. Chem. Abs.* **B**, 1935, 85. British P. 414,918, 1934; *Brit. Chem. Abs.* **B**, 1934, 917; *Chem. Abs.*, 1935, **29**, 1103. French P. 791,011, 1935; *Chem. Abs.*, 1936, **30**, 2807. French P. 762,028, 1934; *Chem. Abs.*, 1934, **28**, 4505.

[72] S. C. Carney, U. S. P. 1,957,818, May 8, 1934, to Shell Development Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 462A; *Chem. Abs.*, 1934, **28**, 4140.

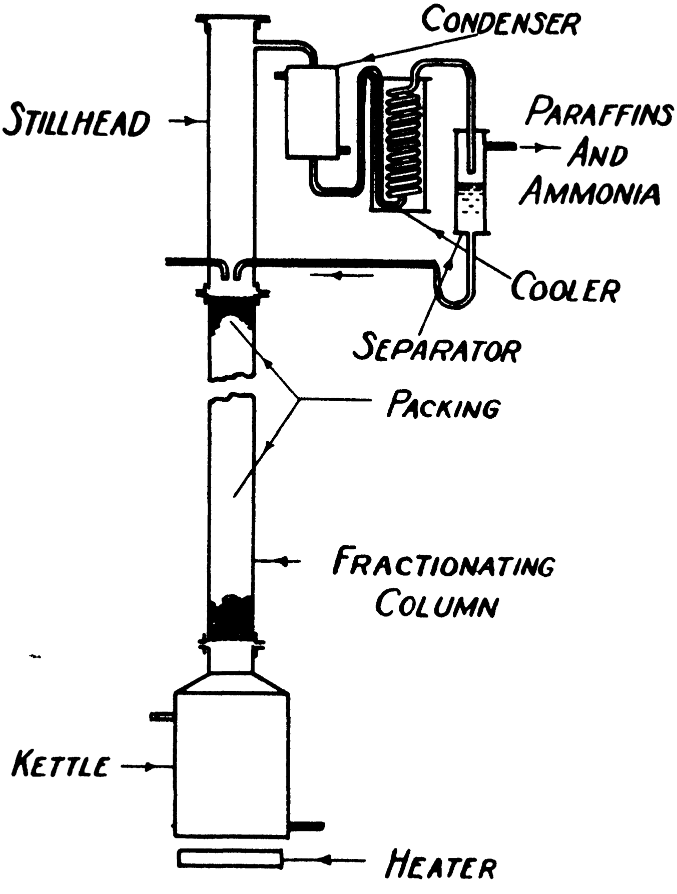

Fig. 52.—Separation of Liquid Olefins from Paraffins by Pressure Fractionation. (R. M. Deanesly)

condensates.[74] Sakmin[75] recommends cooling coke-oven gas with liquid nitrogen and removing (at −150°C.) a fraction rich in ethylene.

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[73] R. M. Deanesly, U. S. P. 1,866,800, July 12, 1932, to Shell Development Co.; *Brit. Chem. Abs.* B, 1933, 1046; *Chem. Abs.*, 1932, 26, 4611.

The possibility of isolating olefins from gas mixtures by absorption in selective solvents has attracted considerable attention. In general, it is proposed to subject the gases, under increased pressure, to countercurrent washing with a solvent, the dissolved olefins being subsequently recovered from the liquid by reducing the pressure or raising the temperature, or both. Processes of this kind are readily made continuous and are attractive from an economic point of view. Voorhees and Youtz[76] suggest compressing cracking gas to 5-10 atmospheres, cooling to 20°C. and washing with an aqueous solution of alcohols, such as methyl alcohol, glycol or glycerol. It is stated that ethylene and propene are 5 to 6 times as soluble as the corresponding paraffins in 95 per cent ethyl alcohol. Bennett[77] proposes dichlorethyl ether, amyl alcohol or isopropyl ether for the selective absorption of olefins at super-atmospheric pressures and relatively low temperatures. The greater solubility of propene in mineral oils is utilized by Horsley[78] in his cyclic process for partial segregation of ethylene from propene. The mixed gases are washed under pressure with a mineral-oil fraction, boiling above 200°C., oil is separated and the pressure is released in stages. The gas from the first stage is recycled. Another method comprises scrubbing the compressed olefin fraction with liquid butane and separating the dissolved olefins by distillation under pressure.[79]

Other media which may serve for extraction of olefins from admixtures containing paraffin hydrocarbons are cresylic acid,[79a] liquid sulphur dioxide,[79b] and a blend of furfurol (65 parts) and toluene (35 parts).[79c]

Certain solutions containing monovalent copper salts appear to exert a preferential solvent action on the lower unsaturated hydrocarbons and this fact is utilized in a number of procedures for the removal of olefins from complex gas mixtures. The preferential solvent action is no doubt due to the formation of double compounds with high dissociation pressure. Tropsch and Mattox[80] found that ethylene (under pressure) and solid cuprous chloride yield an addition compound of the formula $CuCl{\cdot}C_2H_4$, the dissociation pressures of which are 2.14 atmospheres at 0°C., 5.95 atmospheres at 16.8°C., 11.70 atmospheres at 30.0°C. and 19.49 atmospheres at 40.0°C. The addition of less than 10 per cent of kieselguhr to the cuprous chloride increases the rate of absorption of ethylene. Propene under pressure does not react similarly. Ethylene was not absorbed under 60 atmospheres pressure by a suspension of cuprous chloride in cold water.

In the process of Watts,[81] ethylene and higher gaseous olefins are removed from gas mixtures by an ammoniacal cuprous salt solution and the dissolved gases are recovered by heating the solution or reducing the pressure. Horsley[82] proposes ammoniacal solutions of cuprous nitrate, salicylate, phenolate or cresolate for the same purpose. He believes such solutions have a higher absorptive capacity than cuprous chloride or formate.

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[74] W. Wilkinson and J. L. Schlitt, U. S. P. 2,035,516, Mar. 31, 1936, to Air Reduction Co.; *Chem. Abs.*, 1936, **30**, 3443.

[75] P. K. Sakmin, Russian P. 39,311, Oct. 31, 1934; *Chem. Abs.*, 1936, **30**, 3624; *Brit. Chem. Abs.* **B**, 1936, 1137. *Cf. Z. kompr. flüss. Gase*, 1936, **32**, 1, 13; *Chem. Abs.*, 1936, **30**, 5395. *Org. Chem. Ind. (U.S.S.R.)*, 1936, **1**, 145; *Chem. Abs.*, 1936, **30**, 5396.

[76] V. Voorhees and M. A. Youtz, U. S. P. 1,875,311, Aug. 3, 1932, to Standard Oil Co. of Indiana; *Chem. Abs.*, 1932, **26**, 5962; *Brit. Chem. Abs.* **B**, 1933, 853.

[77] H. T. Bennett, U. S. P. 2,026,265, Dec. 31, 1935, to Mid-Continent Petroleum Corp.; *Chem. Abs.*, 1936, **30**, 1220; *Brit. Chem. Abs.* **B**, 1936, 820.

[78] G. F. Horsley, U. S. P. 2,015,223, Sept. 24, 1935, to Imperial Chemical Industries Ltd.; *J. Inst. Pet. Tech.*, 1936, **22**, 54A; *Chem. Abs.*, 1935, **29**, 7635.

[79] R. F. Ruthruff, J. K. Roberts and M. T. Carpenter, Canadian P. 356,810, 1936, to Standard Oil Co. of Indiana; *Chem. Abs.*, 1936, **30**, 3223.

[79a] C. C. Miller, U. S. P. 2,069,172, Jan. 26, 1937, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1937, **31**, 1997.

[79b] C. C. Miller, U. S. P. 2,069,173, Jan. 26, 1937, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1937, **31**, 1997.

[79c] French P. 801,347, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1937, **31**, 416.

[80] H. Tropsch and W. J. Mattox, *J.A.C.S.*, 1935, **57**, 1102; *J. Inst. Pet. Tech.*, 1935, **21**, 298A; *Brit. Chem. Abs.* **A**, 1935, 957; *Chem. Abs.*, 1935, **29**, 5036.

[81] H. G. Watts, U. S. P. 1,977,659, Oct. 23, 1934, to Imperial Chemical Industries Ltd.; *Chem. Abs.*, 1935, **29**, 180. Also British P. 393,317, 1933; *Chem. Abs.*, 1933, **27**, 5756.

One disadvantage of the use of ammoniacal solutions of cuprous salts is the high volatility of ammonia which tends to be carried forward in the gas stream and whose recovery necessitates special equipment. To overcome these difficulties, Joshua and Stanley[83] employ solutions of cuprous salts in a mixture of water and a hydroxyalkylamine, such as monoethanolamine, diethanolamine, propanolamines and butanolamines. These bases are much less volatile than ammonia so that the necessity of an expensive and troublesome recovery system is obviated. It is also desirable to have present a salt of the base, such as the hydrochloride or the formate, in an amount up to about 1 mole of the salt per gram-atom of monovalent copper. A typical solution for absorbing olefins from gas mixtures is prepared by dissolving 100 g. of cuprous chloride in a mixture of 300 g. of water, 200 g. of monoethanolamine and 75 cc. of hydrochloric acid of density 1.16. The solubility of some gases in this solution at 20°C. and at various pressures is given in Table 40, the solubility being expressed in liters of gas at N.T.P. dissolved by 1 kilogram of solvent.

TABLE 40.—Solubility at Absolute Pressures of:

Gas	1 Atm.	5 Atms.	10 Atms.	20 Atms.
Ethylene	8.4	15.8	21.2	24.2
Propene	1.1	4.3	6.1	—
Butenes	1.0	—	—	—
1,3-Butadiene	11.0	—	—	—
Hydrogen	—	—	0.08	0.17

In practice, the gaseous mixture is washed under pressure with a countercurrent stream of the solvent and dissolved hydrocarbons are recovered by reducing the pressure and warming the solution. By this procedure, gases containing 90 per cent, or more, of mixed olefins are obtained. Since the olefins dissolve in cuprous salt solutions with heat evolution, cooling is necessary during the washing operation. Furthermore, acetylene must be removed from the gases prior to absorption, otherwise cuprous acetylide is formed.

The separation and concentration of ethylene from cracking gas by adsorption on charcoal have been recorded by Pipik.[84] This method, however, requires careful control of the temperature. Displacement of ethylene from charcoal is best effected, not with steam, but with cracking gas. A 2 per cent solution of ethylene was concentrated to 17 per cent and a 25 per cent solution to 55 per cent by this procedure.

Partial segregation of gaseous hydrocarbons has been accomplished by Fussteig[85] by the use of active charcoal contained in two towers in series. By passage of cracking gas, previously dried over calcium chloride, through this system it was possible to condense all the ethylene homologues in the first tower and to retain the ethylene in the second. The olefins were desorbed by wet steam, after which

[82] G. F. Horsley, British P. 424,843, 1935, to Imperial Chemical Industries Ltd.; *Chem. Abs.*, 1935, **29**, 5129; *J. Inst. Pet. Tech.*, 1935, 21, 218A; *Brit. Chem. Abs.* B, 1935, 537. French P. 797,490, 1936; *Chem. Abs.*, 1936, **30**, 7120.

[83] W. P. Joshua and H. M. Stanley, U. S. P. 2,005,500, June 18, 1935, to Distillers Co. Ltd.; *Chem. Abs.*, 1935, **29**, 5122. Also British P. 428,106, 1935; *Brit. Chem. Abs.* B, 1935, 617; *Chem. Abs.*, 1935, **29**, 6676. French P. 784,506, 1935; *Chem. Abs.*, 1936, **30**, 106.

[84] O. Pipik, *Azer. Neft. Khoz.*, 1933, No. 2, 80; *Chem. Abs.*, 1934, **28**, 7490; *J. Inst. Pet. Tech.*, 1935, 21, 407A.

[85] R. Fussteig, *Chim. et ind.*, 1936, **35**, 1022; *Chem. Abs.*, 1936, **30**, 5934; *Brit. Chem. Abs.* B, 1936, 677. *Cf.* V. I. Shvemberger, P. I. Dolin, S. S. Zolotarev, N. F. Okhapkina and L. I. Nikolaeva, *Sintet. Kauchuk*, 1935, No. 4, 13; *Brit. Chem. Abs.* B, 1936, 818; *Chem. Abs.*, 1935, **29**, 6744.

it was necessary to regenerate the charcoal with steam superheated to 250°C. Butadiene was removed by absorption in a saturated solution of cuprous chloride, from which it could be recovered by warming to 55-60°C. Also, it has been suggested that the propane and butene from coke-oven gases may be isolated by absorption with active carbon.[86] In this case, benzene and hydrogen sulphide must be removed before absorption.

The use of silica gel, activated by heating at 270-280°C. for 3.5 to 4 hours, for the recovery of butene-2 from air containing small concentrations of that hydrocarbon, has been investigated by Volzhinskii, Globov and Khrenova.[87] At 20°C., with a gas mixture containing about 5 per cent of the hydrocarbon, the gel absorbed about 4 per cent by weight of butene-2. Desorption and regeneration were carried out by heating to 200-225°C. but the gel then exhibited a lower adsorptive power.

It is of interest to note that hydrogen can be removed from gases rich in olefins by selective oxidation with oxygen or air in the presence of a catalyst, such as copper oxide, with practically no simultaneous loss of hydrocarbon constituents.[88] Addition of an oxide of carbon to the gaseous mixture and effecting reaction between the oxide and hydrogen has been proposed also.[89]

PRODUCTION OF ACETYLENE

In the pyrolysis of petroleum hydrocarbons, acetylene formation probably begins at about 700°C. and increases with rising temperature. Largest yields from gaseous hydrocarbons appear to be obtained under the following conditions: (1) high temperatures, e.g., the electric arc, for short periods of time, (2) reduced pressures, and (3) the use of a diluent, such as hydrogen or steam, to minimize decomposition to hydrogen and carbon.[90]

On account of its cheapness and abundance methane has been studied extensively from the viewpoint of acetylene production and the experimental data of numerous investigators have been correlated by Storch.[91] The variation of the equilibrium constant of the reaction

$$2CH_4 \longrightarrow C_2H_2 + 3H_2 - 91{,}000 \text{ cal.}$$

is represented in Fig. 53, in which the data has been calculated from the spectroscopic results of Kassel[92] for the free energies of the hydrocarbons concerned. The value of the constant,

$$K = \frac{P_{C_2H_2} \times P^3_{H_2}}{P^2_{CH_4}}$$

varies from 5×10^{-3} at 1000°C. to 250 at 1500°C. Kinetically, the decomposition of methane under conditions of low hydrogen concentration can be represented by the unimolecular equation

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[86] British P. 449,013, 1936, to Ruhrchemie A.-G.; *J. Inst. Pet. Tech.*, 1936, **22**, 453A; *Chem. Abs.*, 1936, **30**, 7823. French P. 782,840, 1935; *Chem. Abs.*, 1935, **29**, 7055.

[87] I. A. Volzhinskii, V. A. Globov and Z. A. Khrenova, *Sintet. Kauchuk*, 1934, No. 1, 1; *Brit. Chem. Abs.* **A**, 1935, 1348; *Chem. Abs.*, 1935, **29**, 2788.

[88] A. White and P. K. Frolich, U. S. P. 1,911,780, May 30, 1933, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1934, 263; *Chem. Abs.*, 1933, **27**, 4039.

[89] P. K. Frolich, U. S. P. 2,002,534, May 28, 1935, to Standard Oil Development Co; *Chem. Abs.*, 1935, **29**, 4373; *J. Inst. Pet. Tech.*, 1935, **21**, 466A.

[90] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

[91] H. H. Storch, *Ind. Eng. Chem.*, 1934, **26**, 56; *Brit. Chem. Abs.* **B**, 1934, 228; *Chem. Abs.*, 1934, **28**, 1014. For the utilization of methane, see also A. Ya. Kubul'nek, *Neft.*, 1933, 4 (7), 10; *Chem. Abs.*, 1935, **29**, 1966.

[92] L. S. Kassel, *J.A.C.S.*, 1933, **55**, 1351; *Chem. Abs.*, 1933, **27**, 2611; *Brit. Chem. Abs.* **A**, 1933, 561.

$$\log k = 11.864 - \frac{17,352}{T}$$

and this has been shown by Storch to represent quite satisfactorily the data given by other workers.

The influence of contact time on the formation of ethylene and acetylene from methane at 1400°C. and 50 mm. pressure is shown by the results of Tropsch and Egloff.[93] (Table 41.)

TABLE 41.—*Effect of Contact Time on Ethylene and Acetylene Formation.*

Contact Time 10^{-3} Sec.	Gas Analysis Per Cent Vol. C_2H_2	C_2H_4	C_2H_6
2.3	1.6	2.2	nil
5.0	4.6	2.2	nil
6.4	5.0	1.6	nil
14.0	6.0	1.2	nil

The equilibrium constants of the thermal dehydrogenation of ethylene to acetylene

$$C_2H_4 \longrightarrow C_2H_2 + H_2 - 45,800 \text{ cal.}$$

have been calculated by Storch from Kassel's free energy data. The variation of the constant

$$K = \frac{P_{C_2H_2} \times P_{H_2}}{P_{C_2H_4}}$$

with temperature is represented graphically in Fig. 53. The work of Fischer and Pichler[94] seems to indicate that this dehydrogenation is a unimolecular reaction though there is a definite trend towards higher conversions at the lower partial pressures of ethylene. Dilution with hydrogen markedly suppresses polymer formation with the result that acetylene can be made the main reaction product at high temperatures, low pressures and shorter heating periods. Dreyfus[95] reports that ethylene may be converted to acetylene by passage of gas, preheated to 800-1000°C., though an annular space at 1200°C. for a contact period of 0.05-0.01 second, employing hydrogen to reduce the partial pressure of the hydrocarbon to below 1 atmosphere. The results of Fischer and Pichler[96] for the pyrolysis of ethane at low pressures and temperatures of 1000-1400°C. are practically identical with those obtained under the same conditions with ethylene. This probably means that ethane dehydrogenates to ethylene much more rapidly at these temperatures than does ethylene to acetylene.

Pyrolysis of propane, *n*-butane and isobutane at 1100°C. and 50 mm. pressure furnishes considerable amounts of acetylene, the concentration of the latter in the resulting gas increasing with increased contact time.[97]

To obtain substantial yields of acetylene from methane it is necessary to conduct pyrolysis at temperatures as high as 1400-1500°C. and to operate at low partial pressures of methane.[98] In practice, it may not be feasible to carry out this high temperature cracking at pressures below atmospheric so that dilution with a cheap and relatively inert gas would be required for efficient operation. Hydrogen or oxides of carbon have been employed as diluents. When hydrogen is used, Frost[99] points out that a 95 per cent conversion of methane to acetylene can be secured at 1500° absolute and 0.1 atmosphere pressure. From the economic point of view, Storch believes the conversion of methane into acetylene is limited by the necessity of carrying out a highly endothermic reaction at a very high temperature level. Furthermore, the high temperatures needed virtually exclude the use of all constructional material except alundum or silicon carbide. He suggests that the process might be carried out in an intermittent cycle, a checker work of refractory material being first raised to the reacting temperature by burning preheated natural gas and compressed air and then effecting the decomposition of diluted methane in the second stage of the cycle. Storch also points out that conversion of ethylene,

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[93] H. Tropsch and G. Egloff, *Ind. Eng. Chem.*, 1935, **27**, 1063. See also G. Egloff and E. Wilson, *Ind. Eng. Chem.*, 1935, **27**, 917; *Chem. Abs.*, 1935, **29**, 6203; *Brit. Chem. Abs.* **A**, 1935, 1206.

[94] F. Fischer and H. Pichler, *Brennstoff-Chem.*, 1932, **13**, 406; *Brit. Chem. Abs.* **B**, 1933, 53; *Chem. Abs.*, 1933, **27**, 2016.

[95] H. Dreyfus, British P. 440.432, 1935; *Brit. Chem. Abs.* **B**, 1936, 263; *Chem. Abs.*, 1936, **30**, 3836; *J. Inst. Pet. Tech.*, 1936, **22**, 251A.

[96] F. Fischer and H. Pichler, *Brennstoff-Chem.*, 1932, **13**, 406; *Brit. Chem. Abs.* **B**, 1933, 53; *Chem. Abs.*, 1933, **27**, 2016.

[97] G. Egloff and E. Wilson, *Ind. Eng. Chem.*, 1935, **27**, 917; *Chem. Abs.*, 1935, **29**, 6203; *Brit. Chem. Abs.* **A**, 1935, 1206.

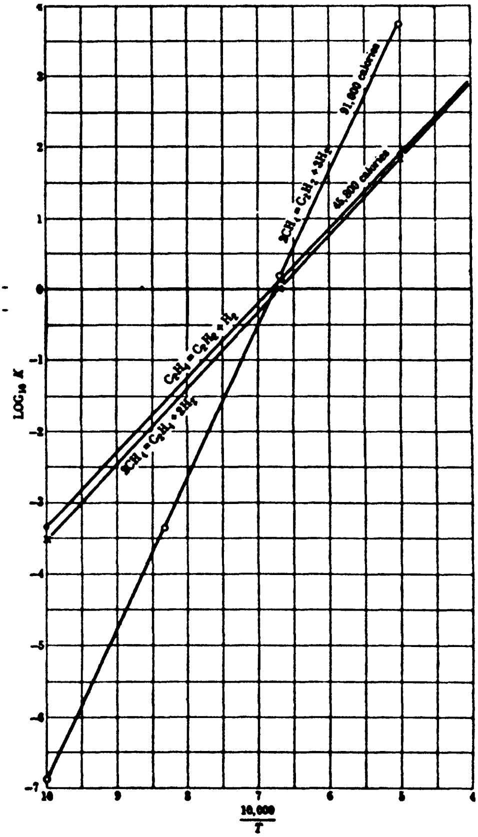

FIG. 53.
Variation of Methane-Ethylene-Acetylene Equilibrium Constants with Temperature. (H. H. Storch)

Courtesy Industrial and Engineering Chemistry

ethane, propane or butane to acetylene by thermal decomposition does not necessitate such high temperatures so that in the case of these higher hydrocarbons the desired temperatures could possibly be obtained with externally heated tubes, for example, tubes of chrome alloy.

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[98] K. Kobayashi, K. Yamamoto, H. Ishikawa and S. Hinonishi, *J. Soc. Chem. Ind. Japan*, 1935, **38**, 550; *Chem. Abs.*, 1936, **30**, 1210.

[99] A. V. Frost, *Materials on Cracking and Chemical Treatment of Products Obtained, Khimteoret (Leningrad)*, 1935, No. 2, 98; *Brit. Chem. Abs.* **B**, 1936, 482; *Chem. Abs.*, 1935, **29**, 5626. *Cf.* H. Dreyfus and W. H. Groombridge, British P. 458,160, 1935, to British Celanese, Ltd.; *Brit. Chem. Abs.* **B**, 1937, 113.

In the technical processes which have been described for the production of acetylene from methane or natural gas, some method of internal heating, such as incomplete combustion, is generally proposed. Thus, Fischer and Pichler[100] prepared acetylene by passing a mixture of methane and oxygen, in proportions insufficient for complete combustion, through a reaction zone at above 1000°C. The reaction time was less than 0.01 second. Under proper conditions the ratio of carbon monoxide to hydrogen in the resulting gas is approximately 1:2 so that, after removal of acetylene, the residual gas may be used for the synthesis of benzine. de Rudder and Biedermann[101] suggest mixing methane (or higher hydrocarbons) and hydrogen with sufficient chlorine to heat the mixture to a temperature of 1200°C. or higher by combustion of the hydrogen in the chlorine, after starting the reaction by auxiliary heating. Dreyfus[102] reacts carbon with methane or hydrogen, or both, at above 1000°C., heat being supplied to the reactants by combustion of part of the gas. For example, finely divided carbon may be blown through a flame of burning methane. Also, it has been suggested that methane and finely divided coke be placed in an electric arc.[103] The latter is maintained at 1500°C., and the gases are conducted through the arc rapidly to insure a short period of contact. Treatment in the arc is followed by a sudden cooling of the products. Wulff[104] has disclosed a process in which natural gas is compressed to a sufficient pressure to raise the temperature to at least 1370°C. The pressure is released so that the gases are held under the specified temperature for less than 0.1 second and the expanded gases are rapidly cooled to a temperature at which acetylene is stable. A partial conversion of natural gas to acetylene may be secured by passage at 980°C.[105] over silicon carbide, after which the gases are quickly removed and cooled.

In the process of Binnie,[106] a gas mixture containing equal volumes of methane and hydrogen chloride is passed through a tube of refractory material at a temperature of 1400-1450°C. and at a space velocity of 6000-9000 volumes per minute. In some instances a small proportion of chlorine, not more than 1 per cent of the volume of hydrocarbon gas, may be employed.[106a] The use of subatmospheric pressures of the order of 0.1 atmosphere or less, in conjunction with temperatures of about 1300°C., is recommended by Tramm and Jung[107] for the conversion of saturated or unsaturated aliphatic hydrocarbons into acetylene. Pyrolysis of methane may be effected by passage through an electrical resistance furnace, forming the reaction chamber, in which the heating resistance is made of material of large internal area such as activated carbon.[108] A contact mass of tungsten, heated by induction, is suggested by Eymann.[109] Fused alumina has been suggested also, particularly as a lining for the heated reaction zone.[109a]

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[100] F. Fischer and H. Pichler, U. S. P. 1,940,209, Dec. 19, 1933; *Brit. Chem. Abs.* B, 1934, 917; *Chem. Abs.*, 1934, **28**, 1353. See Chapter 52.

[101] F. P. I. de Rudder and H. Biedermann, French P. 748,861, 1933; *Chem. Abs.*, 1933, **27**, 5340.

[102] H. Dreyfus, British P. 427,798, 1935; *Brit. Chem. Abs.* B, 1935, 661; *Chem. Abs.*, 1935, **29**, 5855.

[103] French P. 797,626, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 6998. British P. 455,567, 1936; *Chem. Abs.*, 1937, **31**, 1826.

[104] R. G. Wulff, U. S. P. 1,966,779, July 17, 1934, to Wulff Process Co.; *Chem. Abs.*, 1934, **28**, 5640; *Brit. Chem. Abs.* B, 1935, 343.

[105] R. G. Wulff, U. S. P. 2,037,056, April 14, 1936, to Wulff Process Co.; *Chem. Abs.*, 1936, **30**, 3624.

[106] D. Binnie, U. S. P. 2,000,118, May 7, 1935, to Imperial Chemical Industries Ltd.; *Chem. Abs.*, 1935, **29**, 4028.

[106a] H. Tropsch, U. S. P. 2,063,133, Dec. 8, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1937, **31**, 838.

[107] H. Tramm and R. Jung, German P. 605,640, 1934, to Ruhrchemie A.-G.; *Chem. Abs.*, 1935, **29**, 1832. French P. 790,851, 1935; *Chem. Abs.*, 1936, **30**, 2985. U. S. P. 2,047,397, July 14, 1936; *Chem. Abs.*, 1936, **30**, 5840.

In another procedure the hydrocarbons are heated to obtain partial conversion to olefins and the resulting gases then oxidized.[110] For example, a gas consisting mainly of propane is preheated to about 700°C. (to secure about 5 per cent conversion to olefins) and then subjected to partial combustion at temperatures above 1000°C. The products comprise acetylene, ethylene and methane.

SEPARATION AND PURIFICATION OF ACETYLENE

For the extraction of acetylene from dilute gas mixtures, such as those produced by high temperature pyrolysis of hydrocarbons, countercurrent washing with a selective solvent has been usually employed. The scrubbing operation may be conducted under pressure and acetylene is recovered from the liquid by heating and reducing the pressure. Many organic solvents have been proposed for this purpose, including ethers, esters or mixed ether-esters of the polyglycols;[111] an ester of an aliphatic polybasic acid and a monohydric alcohol having 1 to 3 carbon atoms, such as diethyl oxalate;[112] an alkyl carbonate, e.g., diethyl carbonate;[113] and a wide variety of ketones, aldehydes, aliphatic alcohols and their esters, hydrocarbons and chlorinated hydrocarbons.[114] An example of a liquid alicyclic ketone, to be employed as an extraction medium, is cyclohexanone.[115] Lactones, such as butyro- or γ-valero-lactone, have been suggested also.[115a]

The separation of acetylene from gas mixtures containing ethylene, methane and hydrogen, is effected by washing with hexane at −80°C.[116] The dissolved gases are recovered in two stages, by warming the solution first to about −12°C. to remove methane and finally to about 87°C. to evolve ethylene and acetylene together with some hexane vapor. The latter mixture is then fractionated at about −70°C. under 2 atmospheres pressure to furnish pure components. A combination of solvent action (using water or acetone) and low temperature fractionation has also been proposed by Pyzel.[117]

Absorption in liquefied substances, e.g., ammonia or sulphur dioxide, which are gaseous at 15°C. and 1 atmosphere pressure and condensable at a temperature above −100°C., is recommended when a large proportion of hydrogen is present.[118]

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[108] M. Banc, German P. 594,124 and 594,125, 1934, to Ruhrchemie A.-G.; *Chem. Abs.*, 1934, **28**, 3315. *Cf.* W. Grimme, R. Jung and H. Tramm, German P. 624,696, 1936, to Ruhrchemie A.-G.; *Chem. Abs.*, 1936, **30**, 4768.

[109] C. Eymann, U. S. P. 1,957,254, May 1, 1934, to Koppers Co. of Delaware; *Chem. Abs.*, 1934, **28**, 4071; *Brit. Chem. Abs.* **B**, 1935, 85.

[109a] German P. 636,011, 1936, to Ruhrchemie A.-G.; *Chem. Abs.*, 1937, **31**, 580.

[110] British P. 408,934, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5467; *Brit. Chem. Abs.* **B**, 1934, 615. French P. 761,937, 1934; *Chem. Abs.*, 1934, **28**, 4429.

[111] H. P. A. Groll and J. H. Burgin, U. S. P. 1,965,100, July 3, 1934, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 5474; *Brit. Chem. Abs.* **B**, 1935, 393. British P. 400,054, 1933, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1934, 8; *Chem. Abs.*, 1934, **28**, 2166. German P. 606,343, 1934; *Chem. Abs.*, 1935, **29**, 1614; *J. Inst. Pet. Tech.*, 1935, **21**, 99A. French P. 751,284, 1933; *Chem. Abs.*, 1934, **28**, 1058.

[112] G. B. Taylor, U. S. P. 1,996,088, April 2, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 3353; *Brit. Chem. Abs.* **B**, 1936, 437.

[113] F. J. Metzger, U. S. P. 1,900,655, March 7, 1933, to Air Reduction Co. Inc.; *Brit. Chem. Abs.* **B**, 1933, 996; *Chem. Abs.*, 1933, **27**, 2966. British P. 401,531, 1933; *Chem. Abs.*, 1934, **28**, 2371; *Brit. Chem. Abs.* **B**, 1934, 182.

[114] S. Hujio, Japanese P. 109,413, 1935, to The Minister of Navy; *Chem. Abs.*, 1935, **29**, 4218.

[115] M. Müller-Cunradi, O. Eisenhut and H. Schilling, U. S. P. 1,938,083, Dec. 5, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1046.

[115a] R. M. Isham, U. S. P. 2,063,680, Dec. 8, 1936, to Danciger Oil and Refineries, Inc.; *Chem. Abs.*, 1937, **31**, 710.

[116] R. G. Wulff, U. S. P. 1,938,991, Dec. 12, 1933; *Brit. Chem. Abs.* **B**, 1934, 917; *Chem. Abs.*, 1934, **28**, 1364.

[117] D. Pyzel, U. S. P. 1,985,548, Dec. 25, 1934, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 1235; *Brit. Chem. Abs.* **B**, 1935, 1127.

[118] H. Schilling and R. Stadler, U. S. P. 2,029,120, Jan. 28, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 1616.

To separate acetylene from coke oven gas, a mixture of ammonia and acetone[119] is employed at a temperature of −90°C.

Impurities in acetylene, including phosphine and hydrogen sulphide, may be removed by slow passage of the gas over granules prepared by vacuum drying a paste of bleaching powder, lime and a solution of calcium chloride.[120]

Solvents, such as acetone at about −20°C., are recommended as means of eliminating highly unsaturated hydrocarbons, e.g., diacetylene, from gaseous mixtures containing acetylene.[121] In the procedure, acetone is caused to flow countercurrent to a stream of gases (Fig. 54). If the temperature is maintained at −20°C. only diacetylene is said to be dissolved in the ketone. The latter is then withdrawn from the bottom of the scrubbing tower and warmed by heat exchange with gaseous hydrocarbons resulting from a pyrolytic operation. In this manner diacetylene is said to be removed from the acetone. The washing liquor may be further cooled and returned to the system. Additional liquids which may be employed, at temperatures between −80° and 150°C., are hydrocarbons, halogenated hydrocarbons or nitrobenzene.[122] Other procedures involve cooling the mixed gases to about −70°C.[123] or the preferential polymerization of diolefins, or other highly re-

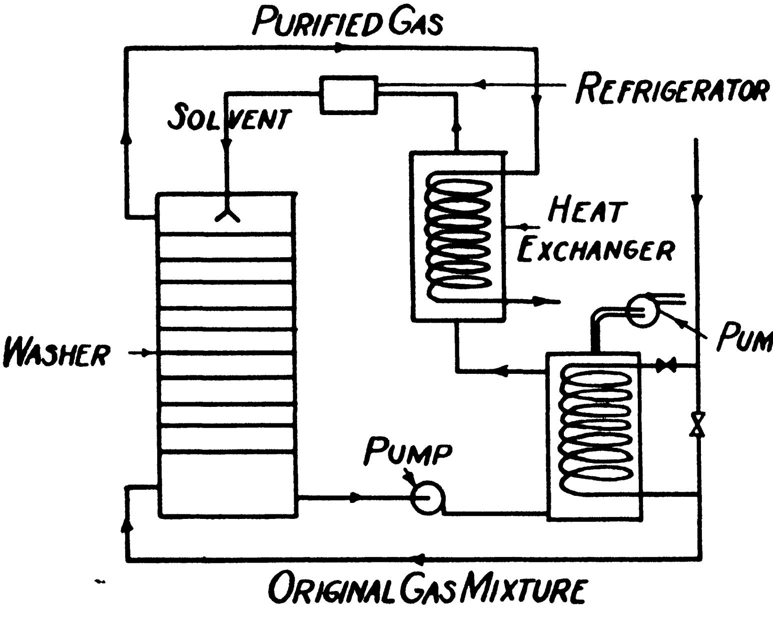

FIG. 54.—Diagram of Method for Separating Diacetylene from Acetylenic Gases. (W. Grimme and H. Tramm)

active hydrocarbons, with silica gel, active carbon, bleaching earths or certain metallic oxides at 200-300°C.[124] Treatment with 60 per cent sulphuric acid containing a dissolved phenol is also suggested.[125]

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[119] G. Fischer, German P. 606,653, 1934, to I. Bronn and Concordia-Bergbau-A.-G.; *Chem. Abs.*, 1935, **29**, 3813.

[120] B. A. Rozhdestvenskii and M. S. Kovalik, *J. Chem. Ind. (Moscow)*, 1935, **12**, 369; *Chem. Abs.*, 1935, **29**, 7938.

[121] W. Grimme and H. Tramm, U. S. P. 1,989,273, Jan. 29, 1935; *Chem. Abs.*, 1935, **29**, 1970; *Brit. Chem. Abs.* B, 1936, 88. See also British P. 415,377, 1934, to Ruhrchemie A.-G.; *Brit. Chem. Abs.* B, 1934, 953; *Chem. Abs.*, 1935, **29**, 913.

[122] P. Baumann, H. Bueckert, W. Sandhaas and H. Schilling, U. S. P. 1,988,032, Jan. 15, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1438.

[123] H. Bueckert, R. Stadler and H. Tanneberger, U. S. P. 1,945,592, Feb. 6, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 2371.

Acetylene is occasionally an objectionable constituent of gases so that it is necessary to eliminate, more or less completely, relatively small amounts of it. This may be accomplished by hydrogenation at low temperature, e.g., 75-90°C., in the presence of a specially prepared catalyst containing nickel and alumina. Olefins are said to be unaffected by this treatment.[126] Another method involves hydrogenation at 250°C., using chromium or nickel compounds as contact agents.[127] Young[128] removes most of the acetylene in olefinic gas mixtures by washing with acetone. The residual acetylene is then completely eliminated by passage of the gases over specially reduced copper at 195°C. The spent catalyst is revivified by conducting air over it at 250°C. and reducing with hydrogen.

Porous fillers, prepared by coagulating a foam resulting from admixture of a cellulose solution and kieselguhr or peat, may be employed in the storing of acetylene.[129]

PRODUCTION OF DIOLEFIN HYDROCARBONS BY PYROLYSIS

Butadiene is an important product of the pyrolysis of many hydrocarbons, especially olefins and cyclohexane derivatives, and may be produced on an industrial scale by thermal decomposition of petroleum hydrocarbons. In addition, other conjugated diolefins are also formed. For example, piperylene (1-methylbutadiene) and also possibly isoprene have been found in the low-boiling liquids from the pyrolysis of kerosene by the Buizov method.[130] However, perhaps the most abundant diolefin (having 5 carbon atoms) is cyclopentadiene, as it has been found in the products obtained on cracking the lower paraffinic hydrocarbons[131] and also in the fraction boiling at 28-50°C. made by the thermal decomposition of kerosene.[132] Dedusenko[132a] determined (by interaction with maleic anhydride) that the portion of gasoline (made by pyrolytic operations at 760°C.) distilling between 20° and 60°C. contained 2.2 per cent of the diolefin. A larger proportion (3.62 per cent) was secured from the cut boiling at 35-40°C.

Butadiene is present in appreciable quantities in cracking gases, particularly those from vapor-phase operation at about 600°C. It is also, in all probability, an intermediate in the conversion of lower paraffins into aromatic hydrocarbons. Thus, the gaseous products obtained in a semi-industrial plant for the manufacture of benzol from Persian natural gas, by cracking at about 800°C., contained 1.08

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[124] F. Zobel and H. Reich, U. S. P. 1,973,840, Sept. 18, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 6726.

[125] A. Auerhahn, U. S. P. 1,960,326, May 29, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 4436.

[126] K. Saurwein, German P. 534,475, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, **26**, 833.

[127] E. Linckh and H. Haeuber, German P. 612,205, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 4776; *J. Inst. Pet. Tech.*, 1935, **21**, 266A.

[128] C. O. Young, Canadian P. 337,317, 1933, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1934, **28**, 1720.

[129] A. Burgeni and R. O. Herzog, German P. 590,497, 1934; *Chem. Abs.*, 1934, **28**, 2166. Also Bloch-Seé and P. Rosemberg, *J. acétylène*, 1935, **95**, 986; *Chem. Abs.*, 1936, **30**, 839. C. D. Hurd, *Ind. Eng. Chem.*, 1934, **26**, 51; *Brit. Chem. Abs.* **B**, 1934, 228; *Chem. Abs.*, 1934, **28**, 1014. O. Lazar, *J. S. African Chem. Inst.*, 1934, **17**, 58; *Chem. Abs.*, 1935, **29**, 317; *Brit. Chem. Abs.* **B**, 1934, 995.

[130] B. A. Kazanskii, A. F. Plate and S. S. Artyunyan, *Sintet. Kauchuk*, 1933, No. 3, 13; *Chem. Abs.*, 1934, **28**, 3567; *Brit. Chem. Abs.* **B**, 1934, 866. See B. V. Buizov, *J. Applied Chem.* (*U.S.S.R.*), 1933, **6**, 1074; *Foreign Pet. Tech.*, 1934, **2**, 185, 213; *Chem. Abs.*, 1934, **28**, 5711.

[131] A. Cambron and C. H. Bayley, *Can. J. Research*, 1934, **10**, 145; *Brit. Chem. Abs.* **A**, 1934, 507; *Chem. Abs.*, 1934, **28**, 2874. S. F. Birch and E. N. Hague, *Ind. Eng. Chem.*, 1934, **26**, 1008; *Chem. Abs.*, 1934, **28**, 6982; *Brit. Chem. Abs.* **B**, 1934, 1049.

[132] I. A. Volzhinskii and A. P. Shcheglova, *Sintet. Kauchuk*, 1933, No. 4, 31; *Chem. Abs.*, 1934, **28**, 3060.

[132a] L. S. Dedusenko, *Bull. acad. sci. U.R.S.S., Classe sci. math. nat. Ser. chim.*, 1936, **59**; *Chem. Abs.*, 1937, **31**, 1992.

per cent of butadiene.[133] Buizov[134] exposed cracking gases to an incandescent platinum wire to secure the same product. Cambron and Bayley[135] studied the aromatization of propane in a high-chromium alloy steel tube and obtained about 5 per cent of the diolefin when operating at 850°C. and at high rates of flow. Pyrolysis of a paraffin wax (melting at 53.2°C.) at temperatures above 650°C. was reported to furnish about 2.5 per cent of the conjugated olefin.[136] The conversion of ethylene into butadiene by cracking in a quartz tube filled with copper gauze and at a temperature of 700° to 750°C. has been studied by Vornov and Voronova.[137] Maximum butadiene recovery per pass was 2-4 per cent but this could be increased to above 10 per cent by 5 consecutive separations and recirculations of the ethylene. The optimum temperature was 750°C. and the use of diminished pressures did not affect the yield. According to Winkler and Häuber,[137a] ethylene admixed with acetylene and conducted at 600°C. through a reaction tube (made of manganese and copper) lined with tin furnishes the diolefin. Other catalysts which may be employed include zinc, aluminum, alloys of these, and brass. Butene-2 has been employed as raw material by Fedorov, Smirnova and Semenov,[138] who obtained a 21 per cent yield by passage of a 7:1 mixture of nitrogen and butene-2 through porcelain tubes at 700°C.; 18-24 per cent of the butene was decomposed per passage. Less conversion to butadiene was secured with zinc oxide, chromic oxide, silica gel, platinum, iron, copper or carbon as catalysts. With magnesium oxide the yields were 25-29 per cent. The chlorination and subsequent dechlorination of butene-2 over barium chloride at 360-400°C. has been investigated by Kazanskii and Rafilzon.[139]

Much better results may be obtained by pyrolysis of cyclohexane hydrocarbons in the presence of 1.5-4 volumes of steam at atmospheric pressure in the absence of catalysts, according to Zelinskii, Mikhailov and Arbuzov.[140] They report the following yields of butadiene, expressed in mole per cent of the hydrocarbon decomposed:—

Hydrocarbon	Temperature °C.	Yield of Butadiene
Cyclohexene	650	65.2
Δ^1-Methylcyclohexene	690	56.4
Cyclohexane	750	39.9
Methylcyclohexane	750	34.8
Ethylcyclohexane	750	41.2
Decalin	750	11.6

Pyrolysis of Δ^1-methylcyclohexene at 690°C. under similar conditions gave 35.3 per cent of isoprene as well as 75.1 per cent of ethylene. Thermic decomposition of chlorcyclohexene in vacuo by an osmium-tungsten filament results in the formation of chlorobutadiene and ethylene.[141] Cyclohexenenitrile may be similarly treated to obtain cyanobutadiene.

[133] W. H. Cadman, *Ind. Eng. Chem.*, 1934, 26, 315; *Chem. Abs.*, 1934, 28, 2499; *Brit. Chem. Abs.* B, 1934, 486.

[134] B. V. Buizov, Russian P. 1102, 1929; *J. Inst. Pet. Tech.*, 1934, 20, 458A.

[135] A. Cambron and C. H. Bayley, *Can. J. Research*, 1934, 10, 145; *Brit. Chem. Abs.* A, 1934, 507; *Chem. Abs.*, 1934, 28, 2874.

[136] S. V. Katzman, *Materials on Cracking and Chemical Treatment of Products Obtained, Khimteoret (Leningrad)*, 1935, No. 2, 93; *Brit. Chem. Abs.* B, 1936, 676; *Chem. Abs.*, 1935, 29, 6031.

[137] F. N. Voronov and A. V. Voronova, *Sintet. Kauchuk*, 1933, No. 3, 5; *Chem. Abs.*, 1934, 28, 3378; *Brit. Chem. Abs.* B, 1934, 819.

[137a] F. Winkler and F. Häuber, German P. 630,952, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, 31, 109.

[138] B. P. Fedorov, A. I. Smirnova and P. A. Semenov, *J. Applied Chem. (U.S.S.R.)*, 1934, 7, 1166; *Brit. Chem. Abs.* A, 1935, 324; *Chem. Abs.*, 1935, 29, 5808.

[139] B. A. Kazanskii and I. A. Rafilzon, *Sintet. Kauchuk*, 1934, No. 1, 1; *Brit. Chem. Abs.* A, 1935, 1480; *Chem. Abs.*, 1935, 29, 3297.

[140] N. D. Zelinskii, B. M. Mikhailov and Yu. A. Arbuzov, *J. Gen. Chem. (U.S.S.R.)*, 1934, 4, 856; *Compt. rend. acad. sci. U.R.S.S.*, 1934, 4, 208; *Chem. Abs.*, 1935, 29, 2152; *Brit. Chem. Abs.* A, 1935, 73.

[141] E. Konrad and O. Bächle, German P. 622,800, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, 30, 3442.

The catalytic decomposition of ethanol, according to the Lebedev[142] process, has been developed on an industrial scale in Russia for the production of butadiene, used as intermediate in the manufacture of synthetic rubber. Ethanol vapor is passed over a special catalyst (a mixture of alumina and zinc oxide) at temperatures of 420-470°C., whereby it is converted into butadiene to the extent of about 20 per cent. Numerous other products are simultaneously formed including pentene, hexene, piperylene, hexadiene, *p*-xylene, toluene, butanol, unsaturated alcohols,[143] aldehydes and ketones as well as methane, ethylene and butenes.[144] Two phenolic compounds, *o*-ethyl phenol and *o*-cresol, have been identified also.[145]

Substitution of *n*-propanol for ethanol results in the formation of about 6 per cent 1,3-dimethylbutadiene as well as some ethylene, propene, methyl-2-pentene and propionaldehyde.[146] When isopropanol is employed, and a catalyst consisting of 15-25 per cent zinc oxide and 75-85 per cent alumina, the main reaction product at 450°C. is said to be propene.[147] Increase of temperature to 580°C. is reported to cause dehydration and dehydrogenation, with a resulting formation of acetone. When 95 per cent of alumina and 5 per cent of zinc oxide was present, the formation of a diolefin, possibly 1,3-dimethylbutadiene-1,3, was observed. Also, it was stated that *sec*-butanol would react to furnish butene-2 at 450°C. with 25 per cent zinc oxide and 75 per cent alumina present. The mechanism of the reaction and the influence of various factors on the yield of butadiene have been described by Lebedev, Gorin and Khutoretzkaya,[148] and also by Smirnov.[149] Some of the liquid hydrocarbons, by-products in the Lebedev process, may be transformed into butadiene by thermal decomposition. Thus, the fraction boiling at 100-150°C. furnished a 15-20 per cent yield of the diolefin by pyrolysis at 550-600°C.[150]

Fractions rich in piperylene and amylene can be recovered from the condensate and the still residues of the catalytic decomposition of alcohols.[151] The condensate is rectified and the part boiling below 60°C. is collected, washed with ice water, treated with calcium chloride, again fractionated, and the portion boiling at 30-45°C. collected. The same procedure is followed with the residues. The fractions thus isolated are mixed and redistilled into cuts boiling at 35-37°C. and 37-40°C. These are treated with bromine, the resulting bromides separated and redistilled from zinc dust and granulated zinc. The products are piperylene (from 37-40°C. fraction) and methylethylethylene (amylene).

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[142] S. V. Lebedev, British P. 331,482, 1929; *Chem. Abs.*, 1931, **25**, 115; *Brit. Chem. Abs.* **B**, 1930, 929. German P. 577,630, 1933; *Chem. Abs.*, 1934, **28**, 481; Russian P. 24,393, 1931 and 35,182, 1934; *Chem. Abs.*, 1934, **28**, 3050; 1935, **29**, 8010; *Chem. Abs.*, 1936, **30**, 4810. A. A. Balandin, *J. Phys. Chem. (U.S.S.R.)*, 1936, 7, 655; *Chem. Abs.*, 1936, **30**, 8147. For description of the laboratory furnace, see S. V. Lebedev, I. A. Volzhinskii, S. G. Kibirklitis, G. G. Koblyanskii, V. P. Krauze, M. A. Krupuishev and Ya. M. Slobodin, *Trudui Gosudarst. Opuit. Zavoda Sintet. Kauchuka Litera B. III. Synthetic Rubber*, 1934, 7; *Chem. Abs.*, 1936, **30**, 4809. A method for determining the yield of butadiene by this process is described by M. I. Danilina, *Sintet. Kauchuk*, 1934, No. 4, 36; *Chem. Abs.*, 1935, **29**, 6205; *Brit. Chem. Abs.* **B**, 1936, 631. See also V. G. Moor and E. K. Kanep, *Materials on Cracking and Chemical Treatment of Products Obtained, Khimteoret (Leningrad)*, **1935**, No. 2, 118, 124; *Chem. Abs.*, 1935, **29**, 5777; *Brit. Chem. Abs.* **B**, 1936, 532.

[143] For preparation of butyl and hexyl alcohols by hydrogenation of the corresponding unsaturated alcohols obtained in the synthesis of bivinyl, see B. A. Kazanskii, A. A. Balandin, I. M. Tzerkovnikov, K. A. Ivanova and E. N. Staroverova, *J. Applied Chem. (U.S.S.R.)*, 1933, **6**, 266; *Chem. Abs.*, 1934, **28**, 2671; *Brit. Chem. Abs.* **A**, 1933, 806.

[144] S. V. Lebedev, *J. Gen. Chem. (U.S.S.R.)*, 1933, **3**, 698; *Chem. Abs.*, 1934, **28**, 3050; *Brit. Abs.* **A**, 1934, 168.

[145] M. V. Likhosherstov, A. A. Petrov and S. V. Alekseev, *J. Gen. Chem. (U.S.S.R.)*, 1934, **4**, 1274; *Brit. Chem. Abs.* **B**, 1935, 442; *Chem. Abs.*, 1935, **29**, 3298.

[146] Yu. A. Gorin and O. M. Neimark, *J. Gen. Chem. (U.S.S.R.)*, 1935, **5**, 1772; *Chem. Abs.*, 1936, **30**, 3402; *Brit. Chem. Abs.* **A**, 1936, 703.

[147] V. P. Krauze and Ya. M. Slobodin, *J. Applied Chem. (U.S.S.R.)*, 1936, **9**, 1278; *Chem. Abs.*, 1936, **30**, 8145; *Brit. Chem. Abs.* **B**, 1936, 970.

[148] S. V. Lebedev, Yu. A. Gorin and S. N. Khutoretzkaya, *Sintet. Kauchuk*, 1935, **4**, No. 1, 8; *Chem. Abs.*, 1935, **29**, 4325; *Brit. Chem. Abs.* **A**, 1936, 311. A theoretical interpretation of the Lebedev synthesis has been advanced by A. A. Balandin (*Acta Physicochim. U.R.S.S.*, 1935, **2**, 363; *Brit. Chem. Abs.* **A**, 1936, 167; *Chem. Abs.*, 1935, **29**, 6494) on the basis of his structure theory of reactions.

[149] N. I. Smirnov, *Sintet. Kauchuk*, **1934**, No. 1, 13; *Chem. Abs.*, 1935, **29**, 3297; *Brit. Chem. Abs.* **B**, 1936, 10.

[150] L. S. Kofman, *Sintet. Kauchuk*, [illegible], No. 3, 7; *Chem. Abs.*, 1935, **29**, 3975; *Brit. Chem. Abs.* **B**, 1936, 535

[151] V. P. Krause, A. M. Kogan and A. V. Kozlovskaya, *Trudi Gosudarst. Opuit. Zavoda Sintet. Kauchuka Litera B. III. Synthetic Rubber*, **1934**, 50; *Chem. Abs.*, 1936, **30**, 4810.

Butadiene may be prepared by dehydration of a mixture of 1,3-butene glycol over solid oxide dehydrating catalysts at temperatures of 160-500°C.[152] An 85-90 per cent yield is obtained by passage of a vaporized mixture of 80 per cent 1,3-butene glycol and 20 per cent water over a catalyst of trisodium phosphate containing 2 per cent free phosphoric acid at 270°C.[153] Cerium phosphate[154] has also been suggested as the contact agent. Instead of using a catalyst in the form of granules, a method of securing it rigidly to the heating surfaces with which the glycol is brought into contact is reported to give better results.[155] Chalmers[156] suggests dehydration of ethylene glycol monoethylether in the gas phase in the presence of metal oxide catalysts, such as alumina or thoria.

RECOVERY AND PURIFICATION OF BUTADIENE

Although distillation may be employed for separating and recovering gaseous hydrocarbons having 4 carbon atoms in their molecules, butadiene cannot be recovered in pure form from such a mixture by fractionation owing to the fact that its vapor pressure is very close to that of isobutene. The use of selective solvents for removing butadiene from other C_4 hydrocarbons has received considerable attention. Promising methods involve the formation of certain addition products, which can readily be resolved into their components by the action of heat.

Procedures for the extraction of butadiene from cracking gases have been reviewed by Markovich and Moor,[157] who recommend the use of selective solvents. It has been found by Moor and Dement'eva[158] that water and aqueous solutions of ethylene chlorohydrin, ethylene glycol, glycerol and acetone as well as of borax, silver nitrate and mercuric acetate were the best extracting media, though a considerable volume and uninterrupted circulation of the liquid were required.[159] However, it appears that butadiene is recovered from the contact gases of the Buizov process, operated industrially in Russia, by liquid absorbents such as kerosene, turpentine and tetralin. According to Smirnov,[160] the absorbent power of ethanol for the diolefin is less than that of kerosene. Absorption in alcohol is said to be effected most economically at a pressure of about 5 atmospheres.[161] Recovery of butadiene from the gaseous products of the Lebedev synthesis is also possible by adsorption in activated carbon, and more than 90 per cent efficiency is said to be attainable by this procedure.[162]

[152] M. Müller-Cunradi, U. S. P. 1,944,153, Jan. 23, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 2012.

[153] W. Reppe and U. Hoffmann, German P. 610,371, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 6244.

[154] W. Reppe and U. Hoffmann, German P. 578,994, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 776.

[155] M. Müller-Cunradi, German P. 601,224, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 7594.

[156] W. Chalmers, German P. 599,503, 1934; *Chem. Abs.*, 1934, **28**, 7268.

[157] M. B. Markovich and V. G. Moor, *Materials on Cracking and Chemical Treatment of Products Obtained, Khimteoret (Leningrad)*, 1935, No. 2, 152; *Chem. Abs.*, 1935, **29**, 6034; *Brit. Chem. Abs.* **B**, 1936, 631. For a method of determining the amount of ethanol in unrectified butadiene, see I. A. Livshitz and V. G. Nazarov, *Sintet. Kauchuk*, **1934**, No. 3, 38; *Chem. Abs.*, 1935, **29**, 6534; *Brit. Chem. Abs.* **B**, 1936, 732.

[158] V. G. Moor and M. I. Dement'eva, *Materials on Cracking and Chemical Treatment of Products Obtained, Khimteoret (Leningrad)*, 1935, No. 2, 157; *Chem. Abs.*, 1936, **30**, 6034; *Brit. Chem. Abs.* **B**, 1936, 631.

[159] V. G. Moor, *Trans. VI Mendeleev Congr. Theoret. Applied Chem.*, 1932, 2 (1), 719; *Chem. Abs.*, 1936, **30**, 2734.

[160] N. I. Smirnov, *Sintet. Kauchuk*, **1933**, No. 6, 5; *Chem. Abs.*, 1934, **28**, 3378; *Brit. Chem. Abs.* **B**, 1934, 823.

[161] Ya. I. Zhigalin, *Sintet. Kauchuk*, **1935**, No. 5, 22; *Chem. Abs.*, 1936, **30**, 429.

[162] G. A. Pankov and A. S. Malinkina, *Sintet. Kauchuk*, 1935, **4**, No. 1, 37; *Brit. Chem. Abs.* **B**, 1936, 228; *Chem. Abs.*, 1935, **29**, 4627.

Butadiene from the catalytic treatment of ethanol by the Lebedev process contains considerable proportions of acetaldehyde as well as of ethers and various hydrocarbons. The aldehyde may be removed almost completely by washing with water.[163]

It has long been known that solutions of cuprous salts will dissolve relatively large amounts of gaseous butadiene. The solubility data of Joshua and Stanley[164] indicate that this diolefin is approximately eleven times as soluble as butene in an aqueous monoethanolamine solution of cuprous chloride. Thus, it was stated that a mixture of butadiene and butene-2 could be resolved by the use of cuprous chloride.[165] One cubic meter of an aqueous solution of the mixed mono- and diolefin is admixed with 200 kg. of cuprous chloride. An additional quantity of neutral aqueous solution of cuprous chloride is then incorporated at 10-15°C. and 1 atmosphere. When the butene-2 has been removed, the butadiene may be separated from the copper complex by heating the latter to 80°C. Van Peski[166] proposes a neutral aqueous solution of a cuprous salt and an alkali metal halide maintained under non-oxidizing conditions by having present (in the solution) reducing agents, such as hydroxylamine. This liquid medium extracts both butadiene and carbon monoxide. It has been shown by Brooks[167] that, under certain conditions, a solid insoluble addition compound is obtained by contacting butadiene with cuprous salt solutions or suspensions. The pure diolefin may be recovered by filtering the precipitate and heating it to about 60°C. According to Brooks this reaction is particularly applicable to the fraction of cracking gas containing hydrocarbons having 4 carbon atoms. The process is carried out by agitating the liquid hydrocarbons and a slurry of solid finely-divided cuprous chloride in water or an aqueous ammonium chloride solution in an autoclave at a temperature below 10°C. Mixing is continued for 1-2 hours after which monolefins are decanted from the butadiene double compound.

In cases where it is desired to eliminate, but not to recover, butadiene and similar compounds from mixtures of such hydrocarbons with monolefins, it is possible to condense the diolefin with various organic materials and to separate the adducts from unchanged monolefins. For example, the diolefins may be combined with benzoquinone, mesityl oxide, maleic anhydride or esters of maleic acid by heating to 100-150°C. The resulting products may be removed from accompanying monolefins by fractionation of the latter. Thus, the cyclic and acyclic diolefins present in hydrocarbon mixtures may be separated by condensation with *p*-quinones, such as α-naphthoquinone, at temperatures below 50°C. whereby addition compounds derived from anthraquinone are obtained. Since different types of cyclic dienes react at different rates, separation of these hydrocarbons from one another is possible by gradual addition of the quinone. For the condensation of acyclic diolefins, the temperature necessary is usually above 50°C.[167a]

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[163] N. I. Smirnov, *Sintet. Kauchuk*, **1933**, No. 1, 13; *Brit. Chem. Abs.* **B**, 1934, 10; *Chem. Abs.*, 1933, **27**, 5052. A. A. Vasil'ev, *Sintet. Kauchuk*, **1933**, No. 5, 5; *Chem. Abs.*, 1934, **28**, 3379; *Brit. Chem. Abs.* **B**, 1934, 823. L. M. Bukreeva-Prozorovskaya and I. M. Tzerkovnikova, *Sintet. Kauchuk*, **1934**, No. 1, 36; *Chem. Abs.*, 1935, **29**, 3297; *Brit. Chem. Abs.* **B**, 1936, 10.

[164] W. P. Joshua and H. M. Stanley, British P. 428,106, 1935, to Distillers Co. Ltd.; *Chem. Abs.*, 1935, **29**, 6901; *J. Inst. Pet. Tech.*, 1935, **21**, 266A; *Brit. Chem. Abs.* **B**, 1935, 617.

[165] I. L. Fridshtein, A. F. Tyul'neva and M. K. Safonova, *Sintet. Kauchuk*, **1935**, No. 3, 13; *Chem. Abs.*, 1935, **29**, 7120; *Brit. Chem. Abs.* **B**, 1936, 945.

[166] A. J. van Peski, U. S. P. 1,999,159, April 23, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 4160. See also Dutch P. 31,454, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 2433. German P. 594,157, 1934; *Chem. Abs.*, 1934, **28**, 3499.

[167] B. T. Brooks, U. S. P. 1,988,479, Jan. 22, 1935, to Standard Alcohol Co.; *Chem. Abs.*, 1935, **29**, 1684; *Brit. Chem. Abs.* **B**, 1936, 88; *J. Inst. Pet. Tech.*, 1936, **22**, 53A.

[167a] British P. 439,491, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 2985; *Brit. Chem. Abs.* **B**, 1936, 180.

It is known that diolefins will combine with sulphur dioxide to yield cyclic sulphones, which are resolved into their components by the action of heat. Perkins[168] suggests reacting hydrocarbon mixtures containing diolefins by heating to temperatures of less than 100°C. (best about 80°C.) under pressure with less than half their weight of sulphur dioxide. The diolefin sulphone is withdrawn from the reaction zone and crystallized.

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[168] G. A. Perkins, U. S. P. 1,993,681, March 5, 1935, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, **29**, 2733; *Brit. Chem. Abs.* B, 1936, 438.

Chapter 5

Production of Aromatic Hydrocarbons by Pyrolysis of Petroleum Hydrocarbons

Aromatic hydrocarbons are obtained by the pyrolysis of practically all other types of hydrocarbons at temperatures of 600-1100°C. On account of their high antiknock values, the lower aromatics, benzene, toluene and xylenes, are valuable constituents of cracked gasolines. The more recent developments in the production of aromatics by cracking have for their object the formation of optimum yields of light benzenoid hydrocarbons for blending with gasolines, and in this respect the lower paraffin hydrocarbons have received special attention since they constitute a cheap and abundant source of raw materials. Aromatization of paraffins and olefins would appear, therefore, to be a promising method for the better utilization of petroleum gases.

As pointed out previously (see Chapter 4), much higher temperatures may be employed in the laboratory for pyrolytic conversions than would be feasible in commercial operations. Furthermore, when the hydrocarbons undergoing treatment are liquids, e.g., kerosene distillates, the gas loss (i.e., the proportion of product obtained as butanes or other hydrocarbons of lower molecular weights) is often high, sometimes as much as 50 to 60 per cent of the charging stock. The application of pressure and the use of catalysts may reduce, at least to some extent, the destructive effects attendant upon the employment of high temperatures.

PRODUCTION OF AROMATIC HYDROCARBONS FROM LIQUID PETROLEUM FRACTIONS

According to Kofman,[1] cracking at 700°C. of the low-boiling (100° to 150°C.) hydrocarbons, from the pyrolysis of alcohol,[2] yields 5.8 per cent benzene, 19.5 per cent toluene and 18.5 per cent xylenes. Kanep[3] found that the proportion of aromatics decreased with increasing boiling range of the charging stock. Thus, he reported that, when cracked at 700°C., a petroleum fraction boiling up to 150°C. gave 20.9 per cent aromatics, that boiling at 150-210°C. yielded 15.6 per cent, while a third cut, distilling at 210-270°C., furnished 12 per cent. At still higher temperatures, e.g., a glowing platinum wire, Kogasin[4] was decomposed into light benzene hydrocarbons (20 per cent) and gaseous products (80 per cent).[5] The latter consisted mainly of unsaturated hydrocarbons.

Vapor-phase cracking of Surakhany paraffinic fuel oil at atmospheric pressure in an iron retort at 650-800°C. has been shown by Butkov, Rabinovich and Kolpenskaya[6] to yield substantial quantities of aromatic hydrocarbons. Within this temperature range the proportion of light products amounted to about 18 per cent. An increase in the cracking temperature raised the yield of benzene but toluene formation attained a maximum of 3.6 per cent and then decreased at higher temperatures. The naphthalene fraction of the products increased with the temperature of pyrolysis and was 2.7 per cent at 800°C. Cambron and Bayley[6a] point out that gasoline containing more than 25 per cent of aromatics is secured by the cracking of petroleum distillates, provided a condition of turbulent flow is maintained in the reaction zone.

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[1] L. S. Kofman, *Sintet. Kauchuk*, 1934, No. 3, 7; *Chem. Abs.*, 1935, **29**, 3975.

[2] Pyrolysis of alcohol to butadiene, for the production of synthetic rubber, is discussed in Chapter 4.

[3] E. K. Kanep, *Materials on Cracking and Chemical Treatment of Products Obtained*, *Khimteoret (Leningrad)*, 1935, No. 2, 71; *Brit. Chem. Abs.* B, 1936, 484; *Chem. Abs.*, 1935, **29**, 5640.

[4] Kogasin is a mixture of hydrocarbons resulting from the reaction of carbon monoxide and hydrogen. See Chapter 52.

[5] F. Fischer, K. Peters and K. Winzer, *Brennstoff-Chem.*, 1935, **16**, 421; *Chem. Abs.*, 1936, **30**, 3991.

In the course of an intensive study of the vapor-phase cracking of various hydrocarbon materials in a KA2 steel tube, using steam as a diluent to minimize carbon production, Groll[7] found that the optimum temperature for aromatic formation was about 800°C. He obtained the following yields by pyrolysis of a refined gas oil, containing originally only small amounts of aromatic constituents.

Temperature °C.	750	800
Yield, gal. per bbl. of charge		
Olefins boiling below 75°C.	0.90	0.95
Benzene	3.03	3.87
Toluene	1.73	1.49
Xylenes and styrene	1.06	0.77
Trimethylbenzenes	1.32	0.52
Higher alkyl-benzenes	....	0.62
Naphthalene	....	12.4
Alkyl naphthalenes	....	8.53
Anthracene and phenanthrene	....	7.35
Alkyl anthracenes, etc.	....	3.82
Heavy tar residue	....	32.6

The influence of temperature on the composition of the light liquid reaction products is very clearly shown by Groll's results. The distillation curve of the liquids made by cracking at 600°C. does not show any plateaus characteristic of aromatic hydrocarbons. At 650°C. near the maximum gasoline yield, the plateaus for the lower aromatics first appear on the distillation curves. At this temperature, benzene, toluene and xylene are present in about equal amounts, though still mixed with much aliphatic hydrocarbons. At 700°C. the aromatics predominate in the light fractions with the yield of benzene exceeding that of toluene, and a smaller amount of xylene. A further increase of cracking temperature causes the gradual disappearance of the aliphatic hydrocarbons and fission of side chains from the alkylated aromatics. These changes are shown by the increasing sharpness of the breaks in the distillation curves and by the increase in the benzene plateau at the expense of those of toluene and xylene.

Aromatics may be obtained by the dehydrogenation of cyclohexane hydrocarbons in the presence of catalysts at relatively low temperatures. Petroleum fractions rich in cyclohexane hydrocarbons may be similarly dehydrogenated under these mild conditions without appreciably altering the other hydrocarbon constituents. Thus, Zelinskii and Shuikin[8] have effected almost complete dehydrogenation of cyclohexanes in fractions of Surakhany gasoline by passage of vapors of the latter together with hydrogen over catalysts of nickel on alumina, or platinum on activated charcoal, at 300°C. The condensates contained over 50 per cent by volume of aromatic hydrocarbons. Catalytic aromatization of Novo-Bogatinsk (Emba) gasoline in the presence of the same catalyst has been investigated also by Zelinskii and Shuikin.[9]

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[6] N. A. Butkov, E. I. Rabinovich and T. P. Kolpenskaya. *Neft. Khoz.*, 1933, **25**, 29; *Chem. Abs.*, 1934, **28**, 302; *Brit. Chem. Abs.* **B**, 1934, 308. See also V. F. Gerr and A. V. Kudinov, *Azer. Neft. Khoz.*, 1935, No. 7, 8, 119; *Chem. Abs.*, 1936, **30**, 6542; *J. Inst. Pet. Tech.*, 1936, **22**, 463A.

[6a] A. Cambron and C. H. Bayley, U. S. P. 2,057,007, Oct. 13, 1936; *Chem. Abs.*, 1936, **30**, 8595.

[7] H. P. A. Groll. *Ind. Eng. Chem.*, 1933, **25**, 784; *Brit. Chem. Abs.* **B**, 1933, 691; *Chem. Abs.*, 1933, **27**, 4063.

[8] N. D. Zelinskii and N. I. Shuikin, *Ind. Eng. Chem.*, 1935, **27**, 1209; *Chem. Abs.*, 1936, **30**, 601; *J. Inst. Pet. Tech.*, 1935, **21**, 448A. *Bull. Acad. sci. U.R.S.S.*, **1935**, 229; *Chem. Abs.*, 1936, **30**, 601; *Brit. Chem. Abs.* **B**, 1935, 1081.

Pyhälä[10] investigated the naphthalene content of the light tar produced (in 50 per cent yield) by cracking Baku crude oil at 650-700°C. Variable proportions of naphthalene were obtained from this material by different methods of recovery, the largest being secured by fractionation in a long iron column whereby additional heating in the vapor phase resulted. Besides naphthalene, Pyhälä isolated two other solid hydrocarbons, melting at 80.5-81.0°C. and 82.5-83.1°C., respectively, which he believed to be labile isomers of naphthalene since they were converted into the latter by heat.

Pyrolysis of paraffin wax (Rangoon) at 450°C. furnishes liquid hydrocarbons which are partly aliphatic and partly cyclic, and analysis of these (by aniline point and refractive index) indicated they contained 1.6-1.7 benzene rings per molecule.[11] When operations are carried out the presence of hydrogen (at a pressure of 100 kg. per sq. cm.) the resulting products contain only 0.4-0.5 benzene rings per molecule. On the other hand, hydrogenation of the wax, using nickel on kieselguhr as a catalyst, prevented cyclization. It thus appears that the latter phenomenon may be controlled or entirely suppressed by choosing the proper conditions of pyrolysis.

PRODUCTION OF AROMATIC HYDROCARBONS FROM THE LOWER PARAFFINS

Because of their cheapness and availability in large amounts, the lower paraffin hydrocarbons have been extensively studied as raw materials for the production of the lower aromatic hydrocarbons. Methane is the preponderating constituent of most petroleum gases but pyrolysis of this hydrocarbon furnishes only small amounts of aromatic liquids even under the best conditions. The average yield of light aromatic oil at temperatures of 1000-1200°C. under optimum conditions of space velocity appears to be about 0.27 gal. per 1000 cu. ft. of methane.[12] The low conversions seem to be due to some extent to the marked inhibiting action of the hydrogen formed during aromatization. If some economic method of removing hydrogen can be found, the total conversion into benzene could be increased to perhaps 50-60 per cent of the methane supplied.[13] It is interesting to note that benzene constitutes about 80 per cent of the *light liquid* from the pyrolysis of methane.

The production of aromatic liquids from methane continues to be a subject of investigation although the reported yields are not superior to those originally procured by Fischer. Thus, Kafuku[14] obtained 3.5 kg. of oil per 1000 cu. ft. of natural gas (containing 94 per cent of methane) by pyrolysis in silica tubes at a temperature of 1000-1050°C. The light oil consisted of 95 per cent of benzene, while the heavy oil had about 50 per cent of naphthalene and 20 per cent of anthracene. Oda's[15] experiments on the decomposition of methane in quartz tubes showed oil yields of the same order as those obtained by Fischer. Dilution of methane with hydrogen or nitrogen greatly reduced these even when larger reaction tubes, higher temperatures and longer heating periods were employed. The formation of aromatic hydrocarbons from Japanese natural gases has also been investigated.[16] Optimum operating conditions with these gases, which are rich in methane, appeared to be a temperature of 1050-1100°C. and a contact time of 0.4-0.5 second. Single-pass operation furnished 87-113 g. of light oil per cubic meter of gas, while recycling gave increased yields but also furnished graphitic carbon and a gas containing 70-80 per cent of hydrogen. Fujio[17] reports 12 per cent of tar containing 23 per cent of benzol and 19 per cent of naphthalene from methane by pyrolysis in quartz or porcelain tubes at 1000-1150°C.

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[9] N. D. Zelinskii and N. I. Shuikin, *J. Gen. Chem. (U.S.S.R.)*, 1934, 4, 901; *Brit. Chem. Abs.* **B**, 1935, 133; *Chem. Abs.*, 1935, **29**, 2721. See also *J. Applied Chem. (U.S.S.R.)*, 1936, **9**, 260; *Chem. Abs.*, 1936, **30**, 5555; *Brit. Chem. Abs.* **B**, 1936, 581

[10] E. Pyhäla, *Petroleum Z.*, 1934, **30** (29), 1; *Chem. Abs.*, 1935, **29**, 1235; *Brit. Chem. Abs.* **B**, 1934, 818; *J. Inst. Pet. Tech.*, 1934, **20**, 487A.

[11] H. I. Waterman, J. J. Leendertse, L. Adam and C. van Vlodrop, *J. Inst. Pet. Tech.*, 1935, 21, 950; *Chem. Abs.*, 1936, **30**, 2738; *J. Inst. Pet. Tech.*, 1936, **22**, 19A.

[12] P. K. Frolich and P. J. Wiezevich, *Ind. Eng. Chem.*, 1935, **27**, 1055; *Brit. Chem. Abs.* **B**, 1935, 980; *Chem. Abs.*, 1935, **29**, 7624.

[13] A. E. Dunstan, E. N. Hague and R. V. Wheeler, *Ind. Eng. Chem.*, 1934, **26**, 307; *Chem. Abs.*, 1934, **28**, 2495; *J. Inst. Pet. Tech.*, 1934, **20**, 319A; *Brit. Chem. Abs.* **B**, 1934, 486.

[14] K. Kafuku, *J. Fuel Soc. Japan*, 1934, **13**, 516; *Chem. Abs.*, 1934, **28**, 5209; *Brit. Chem. Abs.* **B**, 1934, 563.

If the methane decomposition is limited to about 25 per cent and the temperature range kept within 1000° to 1200°C., then according to Smith, Grandone and Rall[17a] the optimum time of contact (Θ) in seconds is expressed by the formula

$$\log_{10}\Theta = \frac{19{,}525}{T} - 15.0967$$

The above relation is based upon the assumption that the pressure in the reaction zone is atmospheric.

The higher homologues of methane furnish much greater amounts of liquid hydrocarbons and at considerably low temperatures. Dustan, Hague and Wheeler[18] obtained the following yields of liquid aromatic hydrocarbons, calculated on gas input, by pyrolysis of the higher paraffins in silica tubes and at a gas flow of about 80 liters per hour per liter of reaction space.

TABLE 42.—*Single Stage Pyrolysis of Paraffin Hydrocarbons at Atmospheric Pressure*

Paraffin	Temp. °C.	% Conversion to Total Liquids	% Conversion to Gasoline below 170°C.	Yield of Light Oil below 170°C. Gallons per 1000 cu. ft.
Ethane	850	17.9	11.2	17.7
	900	21.9	10.6	16.0
Propane	850	23.1	11.7	25.6
Butane	800	20.4	12.9	38.5
	850	24.6	11.6	37.8
Pentane	850	26.8	11.9	—
Hexane	800	33.7	19.2	—
	850	33.8	19.0	—

Results obtained in silica tubes are usually not surpassed when the reaction zones are made of other substances, such as special alloy steels. Materials to be used in the construction of tubes for large production of aromatic hydrocarbons from petroleum gases should be heat-resisting, non-fragile, non-porous, should inhibit carbon deposition, and should catalyze benzene formation. Silica, porcelain, graphite, copper, aluminum, iron, nickel, fireclay and a number of alloys were tested by Dunstan and his co-workers on a laboratory scale but none proved entirely satisfactory. Two of the best alloys were Ferralloy (14 per cent aluminum, 86 per cent iron) and H.R.4 (26 per cent chromium, 0.3 per cent nickel, 1.5 per cent manganese, 0.9 per cent silicon, 0.15 per cent carbon and the remainder of iron). The former was found to be superior to silica in preventing carbon deposition and in favoring benzene production.

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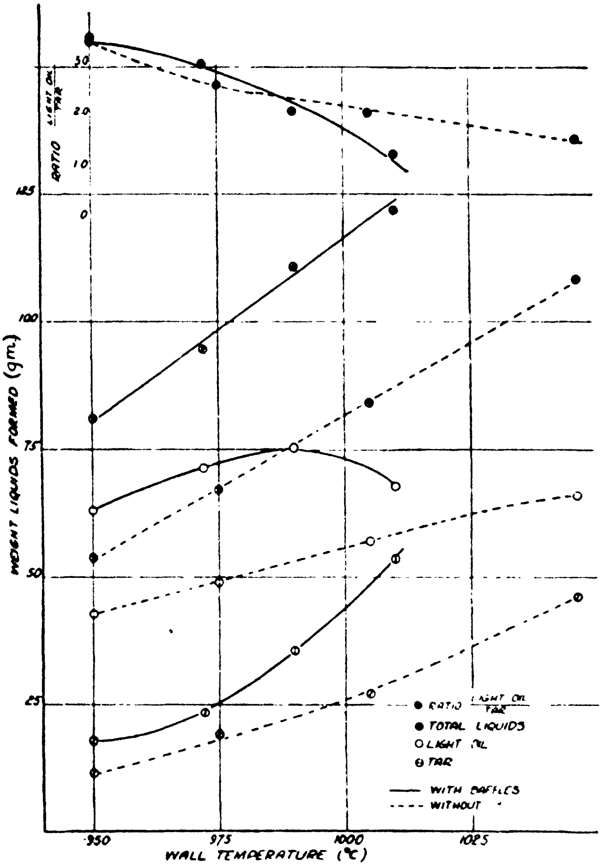
[15] R. Oda, *J. Soc. Chem. Ind., Japan*, 1934, **37**, Suppl. binding, 630; *Chem. Abs.*, 1935, **29**, 1073; *Brit. Chem. Abs.* B, 1934, 261.

[16] K. Kobayashi, K. Yamamoto, H. Ishikawa and S. Hinonishi, *J. Soc. Chem. Ind., Japan*, 1934, **37**, Suppl. binding, 785; *Chem. Abs.*, 1935, **29**, 1959; *Brit. Chem. Abs* B, 1935, 292.

[17] S. Fujio, *J. Fuel Soc., Japan*, 1934, **13**, 435; *Chem. Abs.*, 1934, **28**, 4208; *Brit. Chem. Abs.* B, 1934, 563.

[17a] H. M. Smith, P. Grandone and H. T. Rall, U. S. P. 2,061,597, Nov. 24, 1936; *Chem. Abs.*, 1937, **31**, 710.

[18] A. E. Dunstan, E. N. Hague and R. V. Wheeler, *Ind. Eng. Chem.*, 1934, **26**, 307; *Chem. Abs.*, 1934, **28**, 2498; *J. Inst. Pet. Tech.*, 1934, **20**, 319A; *Brit. Chem. Abs.* B, 1934, 486. *Cf.* D. N. Andreevskii, *Coke and Chemistry (U.S.S.R.)*, 1935, No. 11, 87; *Chem. Abs.*, 1936, **30**, 7536; *Brit. Chem. Abs.* B, 1936, 536.



Courtesy National Research Council of Canada

FIG. 55.—Effect of Turbulent Flow on Liquid Yields in Pyrolysis of Propane and *n*-Butane. (A. Cambron and C. H. Bayley)

The conversion of propane and *n*-butane into aromatic hydrocarbons by pyrolysis at atmospheric pressure in baffled quartz tubes has been investigated by Cambron and Bayley.[10] The advantage of employing conditions of turbulent flow is clearly shown in Fig. 55, in which the yields of liquids at various temperatures from a given tube are compared under conditions of turbulent and stream-line flow, respectively. Pyrolysis of propane in a baffled quartz tube at 950-1000°C. in a single stage operation furnished up to 20 lb. of total liquids and 12 lb. of light oil per 1000 cu. ft. of gas treated. By operating in 2 stages, with inter-stage separation of the liquids, these yields were increased to about 30 lb. of total oil and 20 lb. of light oil per 1000 cu. ft. Later, Cambron and Bayley[20] studied the conversion of propane into aromatic hydrocarbons by pyrolysis in baffled tubes of special heat-resisting alloys. Contrary to the experience of Groll,[21] these investigators observed that chromium-nickel steels of the KA2S type were unsuitable since they markedly catalyzed carbon deposition. However, a nickel-free chromium steel (containing 28 per cent of chromium) did not cause carbon deposition to any appreciable extent. Typical single pass experiments with tubes of the latter material at a temperature of 850°C. gave yields of total liquids aand light oil of 26 lb. and 19 lb., respectively, per 1000 cu. ft. of propane passed. Even better results were secured by recycling part of the exit gas and operating under slight pressure (up to 1 atmosphere). Under these conditions high rates of conversion could be obtained at temperatures as low as 800°C., 23 lb. of light oil together with 10 lb. of liquids boiling above 200°C. being produced per 1000 cu. ft. of propane put through. The composition of the liquids was determined by fractionation and chemical methods. The light oil contained 64 per cent benzene, 14 per cent toluene, 7.8 per cent styrene and small amounts of cyclopentadiene, xylenes and higher aromatics. The liquids boiling above 200°C. contained 25 per cent naphthalene, 12.5 per cent anthracene and smaller amounts of mono- and dimethyl naphthalenes, acenaphthene and phenanthrene.

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[10] A. Cambron and C. H. Bayley, *Canadian J. Research*, 1933, **9** 591; *Brit. Chem. Abs.* **B**, 1934, **308**; *Chem. Abs.*, 1934, **28**, 1506, 1507.

Conversion of the lower paraffin hydrocarbons into liquid hydrocarbons can be effected in two stages, in the first of which the paraffin is pyrolyzed at high temperatures and low pressures to furnish a gaseous product rich in olefins, which is then subsequently polymerized at lower temperatures and high pressures. If aromatic hydrocarbons are desired, the polymerization step should be carried out at moderately low pressures, for example at 30-50 atmospheres and 600-650°C. Much higher yields of liquids are obtained by conducting polymerization at 200 atmospheres pressure and at lower temperatures, for example, 400°C. However, it was noted by Frolich and Wiezevich[22] that the use of the latter conditions causes a change in the chemical composition of the products from the aromatic type obtained at lower pressures to a decidedly non-aromatic material at the higher pressures.

The production of aromatic hydrocarbons from Persian natural gases in a semi-industrial plant has been described in some detail by Cadman.[23] The gases were first freed of hydrogen sulphide and were then conducted through a furnace and thence to a baffled reactor, which was not externally heated. After the heating section, the gas passed to a combined water-spray cooler and tar leg in which the gas temperature was reduced from 800-850°C. to about 90°C. and the bulk of the tar thus separated. After removal of naphthalene and tar fog, the gas was cooled in a series of film coolers and then led to the benzene recovery plant, which was of the usual oil absorption type.[24] A line diagram of the plant (without the desulphurization and refining sections) is shown in Fig. 56. The main line of research resolved itself into the testing of various furnace designs and materials from the viewpoints of satisfactory life at high temperatures, production of benzene and efficiency of heat transfer. Fireclay tubes, though resistant to temperature and non-catalytic as regards carbon formation, were unsuitable on account of poor heat transfer owing to the thickness of wall necessary for mechanical strength. Of the special steels tested, H.R.4 (containing 26 per cent of chromium and only 0.3 per cent of nickel) was the best but even this alloy became brittle on continued use with skin temperatures of 1000-1100°C. Calorized tubes were also tried but had a very short life under the operating conditions. The most satisfactory heating system consisted of a coil of straight lengths of tube with return bends connected by flanges, housed in a gas-fired furnace of the radiant heat type. Various other methods of heating were tried, including surface combustion and submerged flame heating, as well as tests in a recuperator furnace, but none of these proved very satisfactory. The reaction products consisted of carbon, a gas rich in olefins and liquids of an aromatic nature. In the portion of the latter boiling up to 200°C., there was a large fraction (boiling round 80°C.) consisting mainly of benzene together with some cyclohexene. Toluene was the predominating constituent in the cut boiling at 105-115°C. while styrene, *m*- and *p*-xylenes were present in the 135-150°C. fraction. Indene was isolated in the distillate boiling around 180°C. Naphthalene, anthracene and phenanthrene were readily isolated from the tar fraction boiling above 200°C., and the presence of chrysene was indicated.

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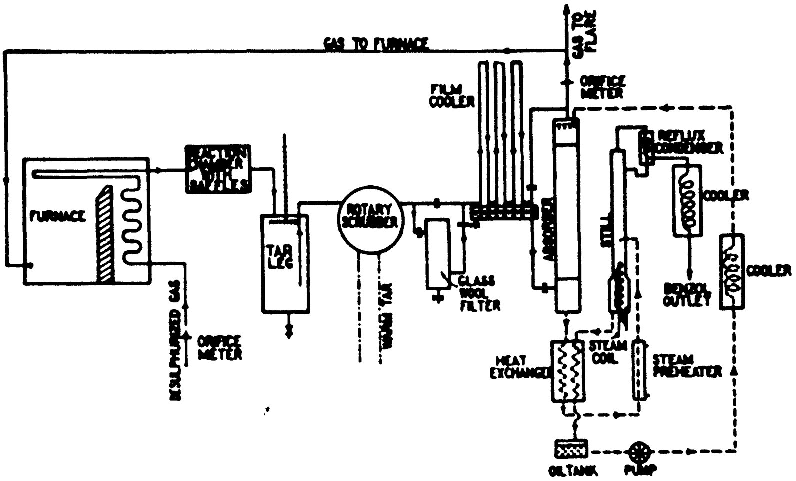
[20] A. Cambron and C. H. Bayley, *Canadian J. Research*, 1934, **10**, 145; *Chem. Abs.*, 1934, **28**, 2874; *Brit. Chem. Abs.* **A**, 1934, 507.

[21] H. P. A. Groll, *Ind. Eng. Chem.*, 1933, **25**, 784; *Brit. Chem. Abs.* **B**, 1933, 691; *Chem. Abs.*, 1933, **27**, 4063.

[22] P. K. Frolich and P. J. Wiezevich, *Ind. Eng. Chem.*, 1935, **27**, 1055; *Brit. Chem. Abs.* **B**, 1935, 980; *Chem. Abs.*, 1935, **29**, 7624.

[23] W. H. Cadman, *Ind. Eng. Chem.*, 1934, **26**, 315; *J. Inst. Pet. Tech.*, 1934, **20**, 319A; *Brit. Chem. Abs.* **B**, 1934, 486; *Chem. Abs.*, 1934, **28**, 2499.

[24] For the recovery of benzol by active carbon, see H. Hollings and S. Hay, *J.S.C.I.*, 1934, **53**, 143; *J. Inst. Pet. Tech.*, 1934, **20**, 325A; *Brit. Chem. Abs.* **B**, 1934, 389; *Chem. Abs.*, 1934, **28**, 2504.



Courtesy Industrial and Engineering Chemistry

FIG. 56.—Line Diagram of Plant for Production of Aromatic Hydrocarbons from Natural Gases. (W. H. Cadman)

Typical crude benzol yields by pyrolysis of various desulphurized Persian natural gases in H.R.4 reaction tubes at surface temperatures of the order of 1000-1050°C. and gas temperatures of 800-900°C. are given in Table 43. Pyrolysis experiments on a semi-technical scale in metal tubes and operating at a pressure of about 30 lbs. per sq. in. gave practically the same benzol yields as those obtained at atmospheric pressure. However, operation under slight pressure was advantageous since heat transfer was improved and throughput increased.

TABLE 43.—*Crude Benzol by Pyrolysis of Natural Gases*

Gas Pyrolyzed	Yield of Crude Benzol, Gallons per 1000 cu. ft.	% Composition of Benzol Benzene Fraction	Toluene Fraction	Styrene and Xylene Fraction
Low-Pressure stripped....	0.96	73.4	5.3	5.8
Low-Pressure unstripped..	1.46	69.1	6.4	7.1
Accumulator............	2.6	70.0	5.5	5.6

The refining of pyrolysis benzol has been briefly discussed by Cadman, who considers that the same general methods as those used for refining coal-tar benzene are also applicable. Sulphuric acid refining was satisfactory in that the refined product was stable and of good quality, although useful unsaturated material is wasted. Vapor-phase refining methods did not prove to be very successful but hydrogenation of such highly unsaturated fractions as the styrene fraction appears promising. Pyrolysis benzene is a good material for the testing of inhibitors.

PRODUCTION OF AROMATIC HYDROCARBONS FROM THE LOWER OLEFINS

Pyrolysis of the lower olefin hydrocarbons at temperatures of 700°C. or above leads to the production of considerable amounts of aromatic liquids. The proportions of such liquids from the lower olefins are considerably greater than those from the corresponding paraffin hydrocarbons, a fact readily explicable on the basis of the theory of aromatic formation, which is developed later. Typical yields of aromatic liquids from the lower olefins by single stage pyrolysis in quartz tubes at rates of flow of about 80 liters per hour per liter of reaction space are summarized[25] in Table 44. These results may be compared with the yields of aromatic liquids obtained by Groll[26] by pyrolysis of various olefin hydrocarbons at atmospheric pressure in KA2 steel tubes and at a rate of flow of 90 liters per hour per liter of tube space. (See Table 45.)

TABLE 44.—*Yield of Liquids by Pyrolysis of Olefins.*

Olefin	Temp. °C.	Conversion to Total Liquids % by Wt.	Conversion to Gasoline % by Wt.	Imp. Gallons of Gasoline Boiling below 170°C. per 1000 cu. ft. of Olefin
Ethylene. .	800	36.1	17.7	1.6
Propene.	750	35.6	20.4	2.75
	800	40.6	19.0	2.5
Butene-1.....	700	35.8	23.6	4.1
	750	39.6	22.5	3.95
Butene-2...	700	37.0	25.8	4.45
	750	39.6	23.2	4.1

The marked catalytic action of certain metals on hydrocarbon decompositions is well illustrated by the work of Hurd and Eilers[27] with ethylene, propene, isobutene, diisobutylene and pentene-2. In the presence of Monel metal, nickel and iron, the production of liquid hydrocarbons by pyrolysis of these olefins at temperatures of 600-700°C. was almost entirely suppressed while carbon formation was pronounced. In general, olefins are more susceptible to the catalytic influence of

[25] A. E. Dunstan, E. N. Hague and R. V. Wheeler, *Ind. Eng. Chem.*, 1934, **26**, 307; *Chem. Abs.*, 1934, **28**, 2498; *J. Inst. Pet. Tech.*, 1934, **20**, 319A; *Brit. Chem. Abs.* B, 1934, 486. See also, A. E. Dunstan and R. V. Wheeler, U. S. P. 1,976,717, Oct. 16, 1934, to Gasoline Products Co.; *Chem. Abs.*, 1934, **28**, 7486; *J. Inst. Pet. Tech.*, 1935, **21**, 26A. See also, C. Candea and E. Macouski, *Bull. sci. école polytech. Timisoara*, 1936, **6**, 305; *Chem. Abs.*, 1936, **30**, 7317.

[26] H. P. A. Groll, *Ind. Eng. Chem.*, 1933, **25**, 784; *Brit. Chem. Abs.* B, 1933, 691; *Chem. Abs.*, 1933, **27**, 4063.

[27] C. D. Hurd and L. K. Eilers, *Ind. Eng. Chem.*, 1934, **26**, 776; *Brit. Chem. Abs.* B, 1934, 792; *Chem. Abs.*, 1934, **28**, 5646; *J. Inst. Pet. Tech.*, 1934, **20**, 493A.

TABLE 45.—*Yield of Aromatics by Pyrolysis of Olefins.*

Olefin	Temp. °C.	Conversion to Total Liquids % by Wt.	Conversion to Benzene, Toluene, Styrene and Xylenes % by Wt.	Gallons of Benzene, Toluene, Xylenes and Styrene per 1000 cu. ft. of Olefin
Ethylene	800 & 825	32.1	15.5	1.6
Propene	775	21.4	—	—
	800	40.0	19.2	3.0
Butene-2	800	30.5	19.2	4.1

these metals than are the corresponding paraffins. Hurd and Eilers found that Ascoloy (a chromium steel containing 24-30 per cent of chromium and 0.21-0.35 per cent of carbon) did not influence the development of carbon from the lower olefins at temperatures of 700°C., and the yields of aromatic liquids obtained with tubes of this metal were similar to those secured with silica and glass. Chromium, molybdenum and lead have been suggested also as contact agents.[28]

The effect of pressure on the production of aromatic hydrocarbons from olefins apparently cannot be deduced from the available kinetic data. However, Dunstan, Hague and Wheeler[29] found no increase in yield of aromatic liquids from ethylene at 600-700°C. when the pressure was raised from atmospheric to 150 lbs. per sq. in. At the higher pressure, however, the working temperature could be reduced by more than 100°C. without loss of yield but increasing the pressure in this temperature region appeared to accelerate the deposition of carbon. On the other hand, Wagner[30] recommends pressures of 500 to 1500 lb. per sq. in. and temperatures of 350-540°C.

PRODUCTION OF AROMATIC HYDROCARBONS FROM CYCLOPARAFFINS

It has long been known that cyclohexane hydrocarbons can be dehydrogenated in the presence of catalysts, such as platinum or nickel, to the corresponding aromatics. This method has been used for the preparation of the latter from petroleum fractions rich in cycloparaffins.[31] The equilibria involved in the transformation of the lower alkylcyclohexanes to the corresponding alkyl benzenes have been investigated by Vvedenskii, Vinnikova, Zharkova and Funduiler.[32] The rate of dehydrogenation of dimethylcyclohexane, at temperatures of 200° to 350°C. and in the presence of nickel or aluminum oxide catalysts, is only slightly greater than that of cyclohexane.[33] Very little methane is formed if the dimethyl derivative is pure.

In the absence of a catalyst, however, it is doubtful whether dehydrogenation is responsible for a large part of the aromatic materials from cyclohexanes on pyrolysis. In the purely thermal decomposition of cyclohexane at atmospheric pressure and at temperatures of about 650°C., the main reaction products appear to be butadiene and ethylene rather than benzene. In the case of cyclohexene,

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[28] French P. 750,869, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1046. British P. 422,273, 1935; *Chem. Abs.*, 1935, **29**, 4373; *Brit. Chem. Abs.* B, 1935, 342.

[29] A. E. Dunstan, E. N. Hague and R. V. Wheeler, *Ind. Eng. Chem.*, 1934, **26**, 307; *Chem. Abs.*, 1934, **28**, 2498; *J. Inst. Pet. Tech.*, 1934, **20**, 319A; *Brit. Chem. Abs.* B, 1934, 486.

[30] C. R. Wagner, U. S. P. 2,028,886, Jan. 28, 1936, to Pure Oil Co.; *Chem. Abs.*, 1936, **30**, 1992.

[31] N. D. Zelinskii and N. I. Shuikin, *Ind. Eng. Chem.*, 1935, **27**, 1209; *J. Inst. Pet. Tech.*, 1935, **21**, 448A; *Chem. Abs.*, 1936, **30**, 601.

[32] A. A. Vvedenskii, S. G. Vinnikova, V. R. Zharkova and B. M. Funduiler, *J. Gen. Chem. (U.S.S.R.)*, 1933, **3**, 718; *Chem. Abs.*, 1934, **28**, 2598; *Brit. Chem. Abs.* A, 1934, 146.

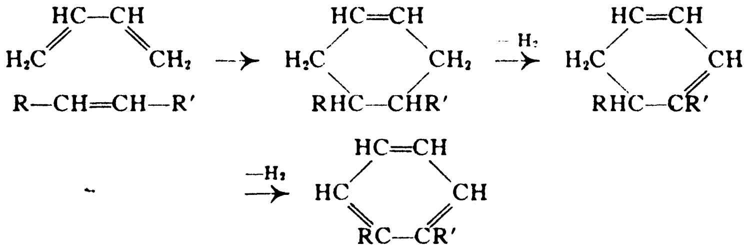
[33] A. A. Balandin and Yu. K. Yur'ev, *J. Phys. Chem. (U.S.S.R.)*, 1934, **5**, 393; *Chem. Abs.*, 1934, **28**, 7127; *Brit. Chem. Abs.* A, 1935, 310. *Cf.* L. Ruzicka and C. F. Seidel, *Helv. Chim. Acta*, 1936, **19**, 424; *Brit. Chem. Abs.* A, 1936, 713; *Chem. Abs.*, 1936, **30**, 6343. Also C. D. Nenitzescu and E. Cioranescu, *Ber.*, 1936, **69**, 1040; *Chem. Abs.*, 1936, **30**, 4824.

Schmidt[34] has shown that rupture of the ring occurs more readily than dehydrogenation. Also, this hydrocarbon does not form more aromatic hydrocarbons than any other olefin.[35] It seems likely, therefore, that the development of aromatics from cyclohexanes in purely thermal processes is the result of secondary decompositions of the ethylene and butadiene initially formed. The available information on the pyrolysis of cyclopentane hydrocarbons indicates that rupture of the ring is the main process and that aromatics are the result of secondary reactions of the olefins produced.

Dehydrogenation of hydroaromatic hydrocarbons in petroleum fractions is said to be effected at 300-500°C. in the presence of vanadium oxide on charcoal.[36] Difficulty reducible oxides or sulphides, such as those of nickel or molybdenum, are suggested also as catalysts,[37] as well as chromium-copper alloys.[38]

MECHANISM OF THE FORMATION OF AROMATIC HYDROCARBONS IN THE PYROLYSIS OF ALIPHATIC HYDROCARBONS

The exact mode of formation of aromatic liquids during the pyrolysis of aliphatic hydrocarbons is still the subject of much controversy. Butadiene is regarded by Wheeler and his co-workers[39] as the essential intermediate which may be produced by dehydrogenation of butene or by combined polymerization and dehydrogenation of ethylene. This diolefin, according to Wheeler's theory, combines with the lower olefins to form cyclohexenes which then dehydrogenate to benzenoid hydrocarbons according to the general scheme:—



In support of this mechanism it was found that equimolecular proportions of ethylene and butadiene react at comparatively low temperatures to give cyclohexene and the latter can be converted to the extent of 25 per cent into benzene at 700°C. Polynuclear aromatic hydrocarbons might be produced similarly by combination of butadiene and cyclohexene with subsequent dehydrogenation of the resulting partly hydrogenated naphthalenes. Dubois[40] also assigns an important role to ethylene as he found pyrogenation of this olefin for 1.5 and 6 minutes at 700°C. yielded almost exclusively aromatics. From these he isolated benzene, toluene, xylene, naphthalene and anthracene.

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[34] O. Schmidt, *Z. Elektrochem.*, 1933, **39**, 975; *Chem. Abs.*, 1934, **28**, 1117; *Brit. Chem. Abs.* **B**, 1934, 51.

[35] H. P. A. Groll, *Ind. Eng. Chem.*, 1934, **26**, 697; *Chem. Abs.*, 1934, **28**, 4580; *Brit. Chem. Abs.* **A**, 1934, 877.

[36] G. F. Horsley, British P. 415,793, 1934, to Imperial Chemical Industries Ltd.; *Chem. Abs.*, 1935, **29**, 1231; *Brit. Chem. Abs.* **B**, 1934, 952; *J. Inst. Pet. Tech.*, 1934, **20**, 581A.

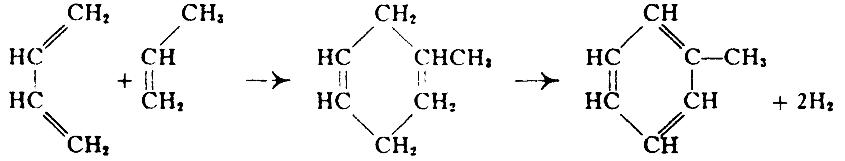
[37] A. Mittasch, M. Pier, R. Wietzel and H. Langheinrich, German P. 627,273, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 3439. British P. 406,808, 1934; *J. Inst. Pet. Tech.*, 1934, **20**, 336A. French P. 760,271, 1934; *Chem. Abs.*, 1934, **28**, 3415.

[38] V. I. Karzhev, V. I. Sever'yanova and A. N. Sivova, *J. Applied Chem. (U.S.S.R.)*, 1936, **9**, 269; *Brit. Chem. Abs.* **A**, 1936, 712; *Chem. Abs.*, 1936, **30**, 5570.

[39] For a review of this theory, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[40] J. Dubois, *Przemysl Chem.*, 1933, 17, 188; *Chem. Abs.*, 1934, **28**, 7490. See also F. I. L. Lawrence, *J. Inst. Pet. Tech.*, 1935, **21**, 790; *Chem. Abs.*, 1935, **29**, 8305; *Brit. Chem. Abs.* **B**, 1935, 979.

Groll[41] advanced a theory which appears to be a development of Berthelot's original concept of the intermediate formation of acetylene and subsequent polymerization of this hydrocarbon. According to Groll, divalent radicals of the type R—C=CH— and —HC=CH— ("nascent acetylene") result from demethanation of the lower olefins and these polymerize directly to aromatic hydrocarbons. It was considered nascent acetylene from demethanation of propene polymerizes to benzene rings more readily than it forms free acetylene. On the basis of this theory therefore, propene is an important intermediate in benzene production, and Groll believed that this was supported by the higher yields of aromatics from propene than from the other olefins. Hague and Wheeler[42] contest this conclusion and state that ethylene, under proper conditions, forms aromatic hydrocarbons to a greater extent than either propene or butene and that the ratio of toluene to benzene in the liquid products from propene is higher than for the other olefins. The high yield of toluene is due to interaction of butadiene and propene.



The assumption of the intermediate formation of divalent unsaturated radicals is not considered by Groll to be essential since acetylene should polymerize so smoothly under the cracking conditions necessary for aromatic production that it may well be an intermediate, though appearing to only a limited extent in the final products. It has been shown by Groll[43] that small quantities of acetylene are actually present in the pyrolytic products from both propane and propene at temperatures as low as 600-650°C.

Perhaps the most important objection which has been raised to Wheeler's theory is that cyclohexene, regarded by Wheeler as the immediate precursor of benzene, has a greater tendency to decompose into equimolecular proportions of ethylene and butadiene than to dehydrogenate thermally to benzene.[44] The yield of aromatic hydrocarbons obtained by cracking cyclohexene at 700°C. is about 46 per cent, of which about half is benzene. On the other hand, it has been shown by Wheeler and Wood, that substantial quantities of cyclohexene are produced by direct combination of butadiene and ethylene. It would seem therefore, that a quasi-equilibrium may exist between butadiene, ethylene and cyclohexene, according to the scheme,

$$C_2H_4 + C_4H_6 \rightleftharpoons C_6H_{10}(\longrightarrow C_6H_6 + 2H_2)$$

and that dehydrogenation of cyclohexene ultimately effects transformation of ethylene and butadiene into aromatics. If the conversion of cyclohexene into benzene is slow compared with the attainment of equilibrium between butadiene, ethylene and cyclohexene, such a scheme would serve to explain why pure cyclohexene decomposes to a considerable extent into ethylene and butadiene, while, on the other hand, pyrolysis of a mixture of ethylene and butadiene forms cyclohexene and aromatic hydrocarbons.

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[41] H. P. A. Groll, *Ind. Eng. Chem.*, 1933, **25**, 784; *Brit. Chem. Abs.* **B**, 1933, 691; *Chem. Abs.*, 1933, **27**, 4063.

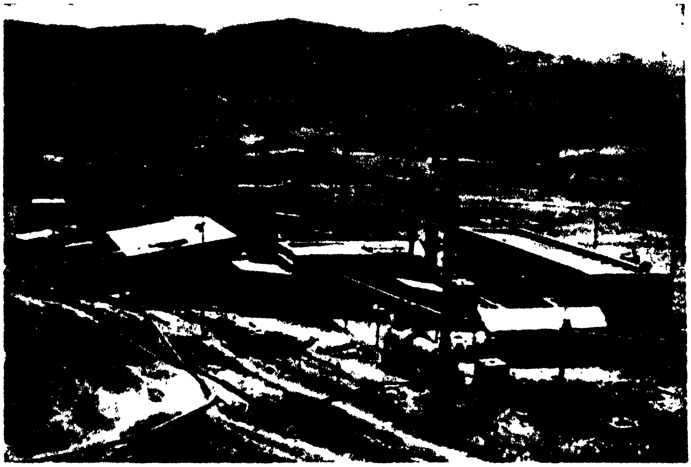
[42] E. N. Hague and R. V. Wheeler, *Ind. Eng. Chem.*, 1934, **26**, 697; *Chem. Abs.*, 1934, **28**, 4579; *Brit. Chem. Abs.* **A**, 1934, 877.

[43] H. P. A. Groll, *Ind. Eng. Chem.*, 1934, **26**, 697; *Brit. Chem. Abs.* **A**, 1934, 877; *Chem. Abs.*, 1934, **28**, 4580.

[44] G. Egloff and E. Wilson, *Ind. Eng. Chem.*, 1935, **27**, 917; *Chem. Abs.*, 1935, **29**, 6203; *Brit. Chem. Abs.* **A**, 1935, 1206.

TECHNICAL PROCESSES FOR THE PRODUCTION OF AROMATIC HYDROCARBONS

The conversion of aliphatic hydrocarbons into aromatics involves heat treatment at temperatures of the order of 700°C. The factors influencing the yield of products include temperature, contact time, pressure and tube material or use of special catalysts. The available experimental data, however, appear to indicate that the yields are little affected by the pressure factor within certain limits, the main advantage being increased throughput of material. Many of the technical processes described are operated at about atmospheric pressure though in some cases inert diluents are employed to reduce the partial pressures of the reactants.



Courtesy Industrial and Engineering Chemistry

FIG. 57.—Development Plant for Production of Aromatic Hydrocarbons from Natural Gases. (W. H. Cadman)

The question of construction material is of prime importance since it is essential that the pyrolysis tubes should be mechanically strong, heat resistant, and nonporous and at the same time should not catalyze carbon formation. Tube walls should be as thin as possible, consistent with mechanical strength, otherwise heat transfer will be poor. This, of course, applies to the case of externally heated reactors which, in spite of some disadvantages, have been generally used. Special heat resisting alloys or tubes coated with heat resisting materials have been proposed. In this connection it is interesting to note that Wheeler[45] points out that materials having stable electronic structures, as shown by high values of electrical and thermal resistance, melting point, tensile strength, hardness and resistance to chemical action, do not catalyze decomposition of hydrocarbons into carbon and hydrogen. He suggests that alloy steels possessing these characteristics should be favored as structural materials in technical processes involving heat treatment of hydrocarbons. A number of such special steels have already been mentioned, the best of these being high chromium steels of low nickel content. However, Harnsberger[46] employed chrome-nickel alloy steels for the production of oil gas by pyrolysis of petroleum fractions at 700-760°C., the carbon deposit being periodically removed from the cracking zone by blowing with steam or air. According to Foster,[47] tubes of an alloy steel containing 25-30 per cent of chromium have been in use for three years in a vapor-phase cracking unit operating at a temperature of 870°C. It has been proposed to suppress still further carbon formation by coating tubes of heat resisting alloys with chromium or molybdenum.[48] Iron tubes covered with chromium or tin are recommended by Porter.[49] Steigerwald[50] reports that both chromium and graphite are useful contact materials for the conversion of natural gas into aromatic hydrocarbons at 800-1200°C.

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[45] T. S. Wheeler, *J. Univ. Bombay*, 1933, **2** (2), 123; *Chem. Abs.*, 1934, **28**, 5322; *Brit. Chem. Abs.* A, 1934, 851.

A number of non-metallic refractory materials have been proposed as contact agents, as for example, chamotte plates or other non-metallic substances coated with silicon.[51] Another procedure is conducting gaseous hydrocarbons at a uniform velocity through a number of straight, unobstructed passages consisting of refractory materials such as chamotte, silicon or silicon carbide.[52] Chambers filled with checker bricks containing silicon carbide, zirconium or magnesite are recommended for effecting the conversion of olefins into aromatic hydrocarbons at elevated temperatures.[53]

Greenstreet[54] converts hydrocarbon gas mixtures into aromatic hydrocarbons by contacting the former at 600-1200°C. with catalysts which do not become coated with carbon. Examples are said to be copper, cobalt, manganese, chromium, molybdenum, tungsten, tin, aluminum, the alkali or alkaline earth metals, silicon, boron, and silica gel. Substances which resist high temperatures, such as the carbides, nitrides, silicides and borides of the above elements, or iron-aluminum alloys, silicon carbide or graphite may be employed. Lustrous carbon is used by Chesny[55] in the conversion of propane-containing gases into liquid hydrocarbons at 900-925°C. Other contact agents for the conversion of gaseous paraffins into benzene hydrocarbons by heat treatment in the absence of steam are the oxides of chromium, tungsten, vanadium or uranium.[56] Bauxite and fuller's earth have been suggested by Towne[57] and also the oxides of aluminum, nickel and zinc,[58] supported on silica gel, pumice, bauxite or activated carbon for the reforming of straight-run gasoline at 500-700°C.[59] Selenium vapors, at 650-950°C., are reported to aid in the transformation of aliphatics (e.g., ethane, propane and butane) into aromatics.[60]

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[46] A. E. Harnsberger, U. S. P. 1,900,057, Mar. 7, 1933, to Pure Oil Co.; *Chem. Abs.*, 1933, **27**, 3063.

[47] A. L. Foster, *Nat. Pet. News*, 1932, **24** (37), 27.

[48] C. Steigerwald, U. S. P. 1,905,520, Apr. 25, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, **27**, 3481.

[49] F. Porter, U. S. P. 1,895,086, Jan. 24, 1933, to Continental Oil Co.; *Brit. Chem. Abs.* **B**, 1933, 903; *Chem. Abs.*, 1933, **27**, 2459.

[50] C. Steigerwald, U. S. P. 1,958,648, May 15, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 4429.

[51] P. Feiler, H. Weigmann and H. Hauber, German P. 578,778, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 776. *Cf.* P. Feiler and H. Weigmann, German P. 634,330, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 8240.

[52] P. Feiler and H. Häuber, U. S. P. 1,967,665, July 24, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5830; *J. Inst. Pet. Tech.*, 1934, **20**, 535A.

[53] P. Feiler, H. Weigmann and G. Hirschberg, U. S. P. 1,973,851, July 18, 1934, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech.*, 1934, **20**, 579A; *Chem. Abs.*, 1934, **28**, 6882. H. Hauber, German P. 583,685, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1046.

[54] C. J. Greenstreet, French P. 762,184, 1934; *Chem. Abs.*, 1934, **28**, 4574. See also, British P. 412,933, 1934; *Chem. Abs.*, 1935, **29**, 593; *Brit. Chem. Abs.* **B**, 1934, 869; *J. Inst. Pet. Tech.*, 1934, **20**, 535A.

[55] H. H. Chesny, U. S. P. 1,965,135, July 3, 1934, to Union Oil Co. of Calif.; *Chem. Abs.*, 1934, **28**, 5655; *J. Inst. Pet. Tech.*, 1934, **20**, 535A; *Brit. Chem. Abs.* **B**, 1935, 343.

[56] E. Linckh and H. Häuber, U. S. P. 1,988,873, Jan. 22, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1832. The oxides of chromium and vanadium have also been recommended by K. E. Skärblom (Swedish P. 84,830, 1935, to Kungl. Arméförvaltningens Artilleridepartement; *Chem. Abs.*, 1936, **30**, 6389) for the conversion of cymene to propene and toluene.

[57] C. C. Towne, U. S. P. 1,943,246, Jan. 9, 1934, to Texas Co.; *Chem. Abs.*, 1934, **28**, 1842; *Brit. Chem. Abs.* **B**, 1934, 917.

[58] C. C. Towne, Canadian P. 334,983, Aug. 15, 1933, to Texaco Development Corp.; *Chem. Abs.*, 1933, **27**, 5531.

[59] C. C. Towne, Canadian P. 335,120, Aug. 22, 1933, to Texaco Development Corp.; *Chem. Abs.*, 1933, **27**, 5529.

The volatile, gaseous fractions, from the stabilization of natural gasoline, may be converted into aromatic hydrocarbons by mixing with 2-5 per cent of steam, preheating the mixture by contact with a hot mass of ferric oxide and then bringing it into contact with more ferric oxide at 538-593°C. Further steam is added to bring the total amount up to 15 per cent and the gases then contacted with an extended surface of metallic iron at 641-704°C.[61] In another process,[62] olefins are preheated to 300-800°F. and then raised to a higher temperature by admixture with hot gaseous combustion products. Afterwards they are passed into a reaction chamber filled with catalytic refractory material, such as fire brick coated with aluminum phosphate, alumina, ferric oxide or thoria. When the olefins contain admixed methane, regulation of the temperature can be effected so that only the unsaturated hydrocarbons are transformed into aromatics.[63] These are separated, and methane is recovered from the residual gas either by liquefaction or by treatment with copper oxide at 150°C. whereby hydrogen (from thermal decomposition of the hydrocarbons) is preferentially oxidized.

Courtesy Industrial and Engineering Chemistry

FIG. 58.—Semi-commercial Pyrolysis Plant for Aromatic Hydrocarbon Production. (W. H. Cadman)

Aromatics may be prepared from butane by maintaining it at a conversion temperature and pressure (470°C. and 3000 lbs. per sq. in., respectively) and adding successive small quantities of olefins.[64] Introduction of the latter should be so regulated that at no time do they constitute more than 5-10 per cent of the hydrocarbon present.

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[60] C. C. Towne, U. S. P. 2,011,385, Aug. 13, 1935, to Texas Co.; *Chem. Abs.*, 1935, **29**, 6606; *Brit. Chem. Abs.* **B**, 1936, 916.

[61] A. Ramage, U. S. P. 1,900,997, Mar. 14, 1933, to M. Wiley and O. L. Smith; *Brit. Chem. Abs.* **B**, 1933, 996; *Chem. Abs.*, 1933, **27**, 3064.

[62] W. W. Odell, British P. 418,779, 1934; *Chem. Abs.*, 1935, **29**, 3143; *Brit. Chem. Abs.* **B**, 1935, 88.

[63] W. Sexauer and S. Loch, German P. 605,432, 1934, to Concordia-Bergbau-A.-G.; *Chem. Abs.*, 1935, **29**, 1103; *J. Inst. Pet. Tech.*, 1934, **20**, 617A. *Cf.* French P. 758,869, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 3078.

A two-stage process comprises first preheating refinery or natural gas to 550°C. and then conducting the products into a second heated, or soaking, zone (650-950°C.) where they are mingled with liquid gasoline or naphtha stock. By maintaining the mixture at the latter temperatures a high anti-knock gasoline is obtained.[65] Lawrence[66] separates still gases into several fractions, one of which is then heated to a temperature at which formation of unsaturated hydrocarbons occurs. The heated fraction, together with an untreated portion, is introduced into a reaction zone in which normally liquid aromatics are developed. The latter are separated and the unreacted gas is recycled. Frey[67] suggests that the volatile hydrocarbons be subjected to a temperature of 750-1200°F. and a pressure of 500-5000 lb. per sq. in. Afterwards the normally liquid products and methane are removed and the residual gases, under a pressure of 500 lb. per sq. in. are conducted through a reaction zone at 1250-1750°F.

MANUFACTURE OF BIPHENYL

The formation of biphenyl by condensation of two molecules of benzene (with elimination of hydrogen) is of technical importance since biphenyl can be used as a heat exchange medium. The preparation of biphenyl from benzene takes place over a wide temperature range, but in practice temperatures of 600-900°C. are usually employed. At 400-500°C. reaction is favored by increased pressures,[68] but commercial methods of manufacture are usually operated at too high temperatures for the application of pressures greater than a few atmospheres. It has been shown by Wibaut and his co-workers[69] that the yield of biphenyl at 420-440°C. under pressures of about 120 atmospheres is increased by catalysts such as hydrogen iodide, iodine and nickel.

At high temperatures, however, reaction is sufficiently rapid in the absence of catalysts for the industrial production, but carbon formation is apparently a troublesome feature and is catalyzed by some materials which are, therefore, to be avoided in continuous operation. Thus, García Banús and Guiteras[70] noted that the decomposition of benzene in the presence of a nichrome wire, heated electrically to 1020-1030°C., results in the deposition of graphite, which lowers the rate of biphenyl formation after a short time. It is reported that carbon formation at a temperature of 800°C. may be inhibited by coating the metal surfaces of the cracking tube with selenium, cobalt sulphide, cobalt, nickel chloride, copper sulphide, silicon, antimony, tin, molybdenum or its sulphides.[71] Williams[72] suggests adding about 0.1 per cent of sulphur, carbon disulphide, hydrogen sulphide or sulphur dioxide to benzene before subjecting it to pyrolysis.

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[64] F. E. Frey, U. S. P. 2,002,394, May 21, 1935, to Phillips Petroleum Co.; *Chem. Abs.*, 1935, **29**, 4373; *J. Inst. Pet. Tech.*, 1935, 21, 267A.

[65] British P. 406,326, 1934, to Texaco Development Corp.; *Chem. Abs.*, 1934, **28**, 4900; *Brit. Chem. Abs.* **B**, 1934, 391.

[66] F. I. L. Lawrence, U. S. P. 1,963,092, June 19, 1934, to Atlantic Refining Co.; *Chem. Abs.*, 1934, **28**, 4896. See also French P. 797,670, 1936, to Alco Products Inc.; *Chem. Abs.*, 1936, **30**, 7325.

[67] F. E. Frey, U. S. P. 2,038,834, Apr. 28, 1936, to Phillips Petroleum Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 264A; *Chem. Abs.*, 1936, **30**, 4312.

[68] J. P. Wibaut, H. M. Romijn and H. D. T. Willink, *Rec. trav. chim.*, 1934, **53**, 584; *Brit. Chem. Abs.* **A**, 1934, 763; *Chem. Abs.*, 1934, **28**, 4725.

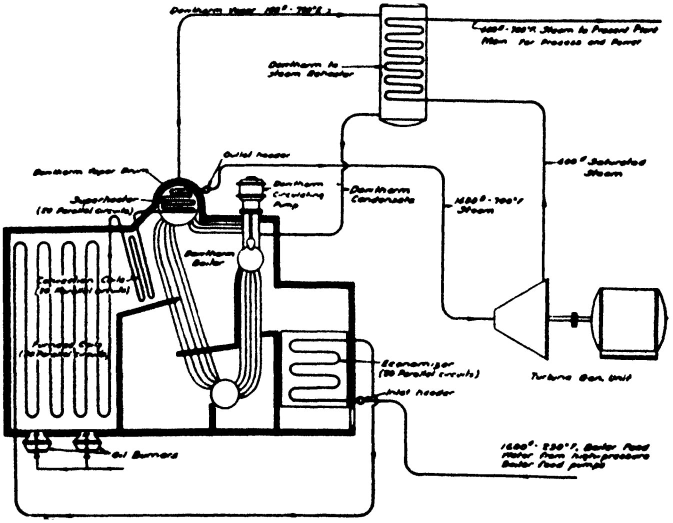
[69] J. P. Wibaut, H. M. Romijn and H. D. T. Willink, *Rec. trav. chim.*, 1934, **53**, 584; *Brit. Chem. Abs.* **A**, 1934, 763; *Chem. Abs.*, 1934, **28**, 4725.

[70] A. García Banús and J. Guiteras, *Anales, soc. españ. fis. quim.*, 1933, **31**, 255; *Brit. Chem. Abs.* **A**, 1933, 1042; *Chem. Abs.*, 1933, **27**, 2948.

[71] J. E. Moose and W. N. Pritchard, U. S. P. 1,968,154, July 31, 1934, to Swann Research, Inc.; *Chem. Abs.*, 1934, **28**, 5834; *Brit. Chem. Abs.*, **B**, 1935, 621.

[72] W. H. Williams, U. S. P. 1,978,069, Oct. 23, 1934, to Dow Chemical Co.; *Chem. Abs.*, 1935, **29**, 182. See also, U. S. P. 1,976,468, Oct. 9, 1934; *Brit. Chem. Abs.* **B**, 1935, 840; *Chem. Abs.*, 1934, **28**, 7263.

A number of specific catalysts have been proposed for the production of biphenyl. One example of such is a neutral silicate of aluminum or magnesium, free from alkali metal compounds.[73] Drossbach and Roell[74] suggest an alkali metal oxide or oxides of thorium, cobalt, tungsten or aluminum. A catalyst consisting essentially of at least one difficultly reducible metal oxide, superficially coated with lustrous carbon, has also been recommended.[75] Instead of employing externally heated reaction chambers, Williams[76] decomposes benzene in a tubular, electrically heated element of graphite or silicon carbide at 650-950°C., the vapors to be pyrolyzed being preheated on the outer surface of the element. Or the volatilized benzene hydrocarbons are conducted through a heated steel tube under conditions of turbulent flow.[77]



Courtesy Industrial and Engineering Chemistry

FIG. 59.—Flow Diagram of Steam Boiler Unit Employing Dowtherm for Indirect Superheating and Reheating of Steam. (D. H. Killeffer)

In the process developed by Reilly,[78] benzene vapor (preheated to about 650°C.) is intimately mixed with about 2 parts by weight of steam (superheated to 1050-1100°C.). The resulting mixture, which is at a temperature of 800-950°C., is conducted through a steel reactor coated internally with a film of magnetic iron oxide. The yield of biphenyl from a single-stage operation may be as high as 30 per cent, this representing 90-95 per cent of the benzene reacting. Passage of benzene through molten inorganic salts at 750-850°C. is said to produce less carbonaceous by-products than when molten lead is used.[79]

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[73] E. Tschunkur and W. Klein, U. S. P. 1,957,988, May 8, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 4068.

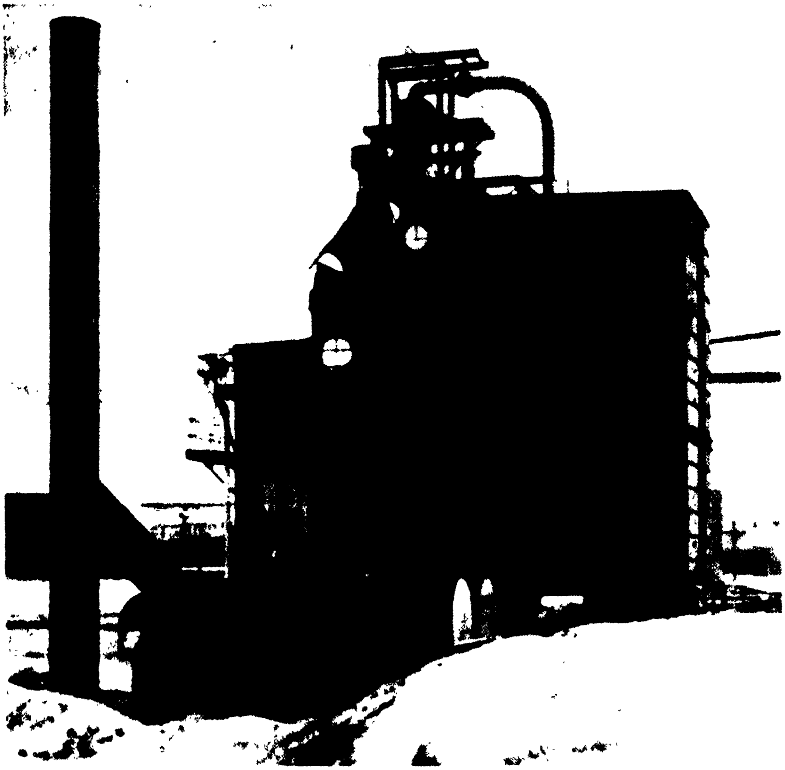
[74] O. Drossbach and E. Roell, U. S. P. 1,996,738, Apr. 9, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 3351 German P. 548,762, 1933; *Chem. Abs.*, 1934, **28**, 1052.

[75] O. Drossbach and E. Roell, U. S. P. 1,996,739, Apr. 9, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935; **29**, 3351. German P. 586,878, 1933; *Chem. Abs.*, 1934, **28**, 1360.

[76] W. H. Williams, U. S. P. 1,925,784, Sept. 5, 1933, to Dow Chemical Co.; *Chem. Abs.*, 1933, **27**, 5341; *Brit. Chem. Abs.* **B**, 1934, 618. U. S. P. 1,981,015, Nov. 20, 1934, to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1935, 939; *Chem. Abs.*, 1935, **29**, 409.

[77] J. N. Carothers, U. S. P. 1,907,498, May 9, 1933, to Swann Research, Inc.; *Brit. Chem. Abs.* **B**, 1934, 87; *Chem. Abs.*, 1933, **27**, 3481.

[78] J. H. Reilly, U. S. P. 1,938,609, Dec. 12, 1933, to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1934, 825; *Chem. Abs.*, 1934, **28**, 1365.



Courtesy Industrial and Engineering Chemistry

FIG. 60.—Exterior Side View of Dowtherm Power Unit. (D. H. Killeffer)

Diaryl hydrocarbons are refined by treatment with an agent, such as concentrated sulphuric or phosphoric acid.[80]

On account of its thermal stability, biphenyl is finding considerable application as a heat-transfer medium, especially in the form of a low melting mixture with diphenyl ether (containing 26.5 per cent of biphenyl). This medium on continued exposure to air at temperatures of about 650°F. undergoes slight oxidation but in other respects is very stable.[81] Its use in a high-pressure steam boiler plant has been described by Killeffer.[82] In addition to diphenyl ether, naphthalene and diphenylamine or aniline may be incorporated with biphenyl.[83] The resulting composition should have a freezing point not higher than 6°C. It is interesting to note that biphenyl and diphenyl ether have been recommended as ingredients of a lubricant employed at high temperatures.[84]

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[79] T. E. Warren and C. B. Durgin, U. S. P. 1,891,514, Dec. 20, 1932, to Swann Research, Inc.; *Brit. Chem. Abs.* **B**, 1934, 11; *Chem. Abs.*, 1933, **27**, 1896.

[80] German P. 586,800, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1353.

[81] R. L. Heindel, Jr., Meeting of Amer. Inst. Chem. Engrs., New York, May, 1934; *Chem. Abs.*, 1934, **28**, 3811. This mixture is known as Dowtherm A. For a comparison of mercury and biphenyl as heat-transfer media, see C. A. Hulsart, *Refiner*, 1934, **13**, 266; *J. Inst. Pet. Tech.*, 1934, **20**, 530A; *Chem. Abs.*, 1934, **28**, 6215. For a comparison of mixtures of chlorinated benzene and biphenyl as heat-transfer media, see F. D. Snell, *Ind. Eng. Chem.*, 1937, **29**, 89; *Chem. Abs.*, 1937, **31**, 910.

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[82] D. H. Killeffer, *Ind. Eng. Chem.*, 1935, **27**, 10; *Brit. Chem. Abs.* B, 1935, 577; *Chem. Abs.*, 1935, **29**, 853. E. F. Holsen, *Ind. Eng. Chem.*, 1936, **28**, 691; *J. Inst. Pet. Tech.*, 1936, **22**, 442A; *Chem. Abs.*, 1936, **30**, 4727.

[83] O. D. Lucas, U. S. P. 1,941,014, Dec. 26, 1933, to Whessoe Foundry and Engineering Co., Ltd.; *Chem. Abs.*, 1934, **28**, 1519. French P. 778,241, 1935; *Chem. Abs.*, 1935, **29**, 4485.

[84] H. H. Dow, U. S. P. 1,918,593, July 18, 1933, to Dow Chemical Co.; *Brit. Chem. Abs.* B, 1934, 567; *Chem. Abs.*, 1933, **27**, 4919.

Chapter 6

Action of Aluminum Chloride on Hydrocarbons

Aluminum chloride has long been known to exert a profound disintegrating and rearranging action on all types of hydrocarbons at relatively low temperatures but it is only within the last few years that the mechanism of such processes has received attention. Indications are that the chemical reactions involved comprise rupture of carbon chains, isomerization and polymerization, and that frequently all take place simultaneously. The practical applications of the action of aluminum chloride on hydrocarbons are (1) the production of gasoline from high boiling petroleum fractions, (2) the formation of higher boiling products, including hydrocarbons having lubricant properties, from olefin hydrocarbons, and (3) the synthesis of resinous materials from cracked distillates. The industrial future envisaged for gasoline made by cracking petroleum in the presence of aluminum chloride does not appear to have materialized. This is partly due to the fact that gasolines produced in this manner have relatively low antiknock values and are therefore not as satisfactory as those formed by thermal cracking operations.

Besides aluminum chloride, other anhydrous inorganic halides including boron trifluoride, tin tetrachloride or zinc chloride have been suggested both as catalysts for the preparation of gasoline and also for polymerizing unsaturated hydrocarbons. The action of such halides will be briefly described in this chapter, with particular attention to aluminum chloride from an industrial viewpoint.

PRODUCTION OF GASOLINE WITH ALUMINUM CHLORIDE

Processes employing aluminum chloride in cracking higher petroleum fractions to gasoline have usually been carried out at temperatures of about 300°C. and under sufficient pressure to avoid excessive volatilization of the chloride. Much information regarding the chemical composition of such gasolines is available from the researches of a number of Russian technologists. Thus, Zelinskii and Mikhlin[1] obtained a 48 per cent yield of gasoline, consisting of paraffin, naphthene and aromatic hydrocarbons, by cracking Emba crude petroleum with 10 per cent of aluminum chloride at atmospheric pressure. Treatment of Grozny paraffin at 130-140°C. was found to give 55 per cent of a colorless distillate of which the fraction boiling up to 150°C. contained only 3 to 4 per cent of aromatic hydrocarbons, corresponding to the dehydrogenated naphthenes, the remainder being paraffins. Gasoline (42 per cent yield) from cracking ceresin in the presence of aluminum chloride contained 2 per cent of aromatics and some naphthenes, while the light kerosene was mainly naphthenic. Zelinskii and Mikhlin noted that when only small proportions of the halide were used unsaturated hydrocarbons appeared in the cracked products.

The decomposition of a Rumanian kerosene by this means has been studied by

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[1] N. D. Zelinskii and N. E. Mikhlin, *J. Applied Chem. (U.S.S.R.)*, 1933, 6, 16; *Foreign Petroleum Tech.*, 1933, 1, 8; *J. Inst. Pet. Tech.*, 1934, 20, 363A; *Chem. Abs.*, 1933, 27, 5176.

Candea, Kühn and Manughevici.[2] They found that reaction begins even in the cold, is more marked on heating and is very pronounced under moderate pressures. Tests carried out at temperatures up to 370°C. gave 24 per cent of light liquid and gaseous products boiling up to 150°C. The application of pressures of 10-40 atmospheres caused an increase to 40 per cent in the yield of light fractions. It was noted that the reaction took place at lower temperatures and pressures when a copper autoclave was employed.

From experiments on the cracking of kerosene, spindle, automobile and cylinder oils with 10 per cent of aluminum chloride, Borisov, Gaverdovskaya and Epifanskii[3] concluded that it was largely the naphthene hydrocarbons which were attacked. These were decomposed by the splitting off of side chains (afterwards appearing as paraffin hydrocarbons), by partial dehydrogenation with formation of aromatic hydrocarbons and by rupture of the ring system to yield paraffins and highly condensed hydrocarbons of the type of asphaltenes and carbenes. That aromatic hydrocarbons are present in the low-boiling fractions resulting from the action of the halide on petroleum distillates has also been shown by Dobryanskii and Zelenin.[4] A typical gasoline formed in this way was found to contain 2 per cent benzene, 5.4 per cent of toluene and 5.7 per cent of xylene, while the gas evolved was principally butane. Zudilov[5] obtained stable gasoline fractions by the action of 10 to 15 per cent of catalyst on the higher fractions of primary tar from sapropelite, the yields varying from 40 to 70 per cent.

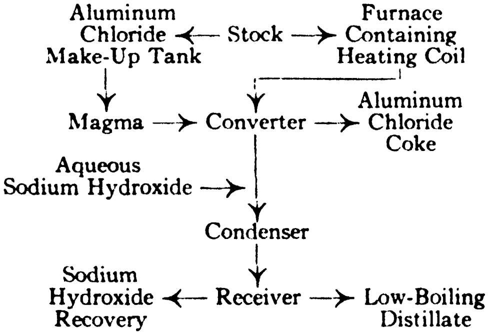

FIG. 61.—Flow Scheme for Cracking Petroleum Fractions with Aluminum Chloride Catalyst. (A. M. McAfee)

Instead of adding freshly prepared aluminum chloride to the petroleum fraction, the catalyst may be generated *in situ*. This was achieved by Galle[6] on adding the metal, previously activated by treatment with mercuric chloride, to petroleum and passing a current of dry hydrogen chloride through the mixture. Apparently a very active form of metallic chloride is produced, for by treating a petroleum fraction (boiling 155° to 300°C.) in this manner, an almost quantitative yield of gaso-

[2] C. Candea, J. Kühn and C. Manughevici, *14me Congr. chim. ind.*, Paris, Oct., 1934; *Chem. Abs.*, 1935, **29**, 6410.

[3] P. P. Borisov, M. V. Gaverdovskaya and P. F. Epifanskii, *Neft. Khoz.*, 1935, **17** (1), 74; *Chem. Abs.*, 1935, **29**, 4926.

[4] A. F. Dobryanskii and N. I. Zelenin, *Khim. Tverdogo Topliva*, 1933, **4**, 606; *Chem. Abs.*, 1934, **28**, 6289; *Brit. Chem. Abs.* **B**, 1935, 54.

[5] I. E. Zudilov, *Khim. Tverdogo Topliva*, 1932, **3**, 129; *J. Inst. Pet. Tech.*, 1935, **21**, 58A; *Chem. Abs.*, 1934, **28**, 5633.

[6] E. Galle, *Petroleum Z.*, 1934, **30** (8), 1; *Brit. Chem. Abs.* **B**, 1934, 390; *Chem. Abs.*, 1934, **28**, 3880.

line is said to have been attained. The latter consisted of a mixture of paraffins, aromatics and naphthenes but no unsaturated hydrocarbons. The degree of amalgamation of the aluminum must be carefully controlled to give the optimum effect. In this connection it is interesting to note that high boiling hydrocarbons may be cracked by first halogenating at a temperature between 0° and 150°C. and then treating (at 100-150°C.) with aluminum which has previously been activated by immersion in a solution of a salt of a less electro-positive metal.[7]

Some details of a procedure for cracking high boiling petroleum fractions have been disclosed by McAfee.[8] The charging stock, (which should contain a high proportion of naphthenes), is heated to just below the temperature of incipient thermal decomposition, e.g., 315 to 400°C., and about 2 per cent of aluminum chloride is added in the form of a heated mixture containing 80 per cent of the catalyst and 20 per cent of oil. The mixture passes to a converter, which is not heated and in which an approximately constant oil level is maintained, and reaction is allowed to take place under a pressure of 75 to 300 lbs. per sq. in. The vapors leaving the reactor are sprayed with an aqueous solution of caustic soda prior to condensation. The coke which builds up in the reaction chamber may be removed periodically by cooling to below 100°C. and washing out with water or aqueous alkali. A somewhat similar cracking process has been described by Jenkins and Stratford,[9] who employ 2 to 10 per cent of an aluminum chloride-hydrocarbon catalyst and effect reaction under pressure and at a temperature (about 482°C.) at which conversion takes place almost instantaneously. To obviate corrosion in processes of this type, Stratford[10] subjects oils, which normally tend to liberate hydrogen chloride with these catalysts, to a preliminary treatment with the halide at a temperature substantially below that at which decomposition of the oil occurs but sufficiently high to effect release of the corrosive substances. An apparatus for refining petroleum utilizing metallic halides has been described by

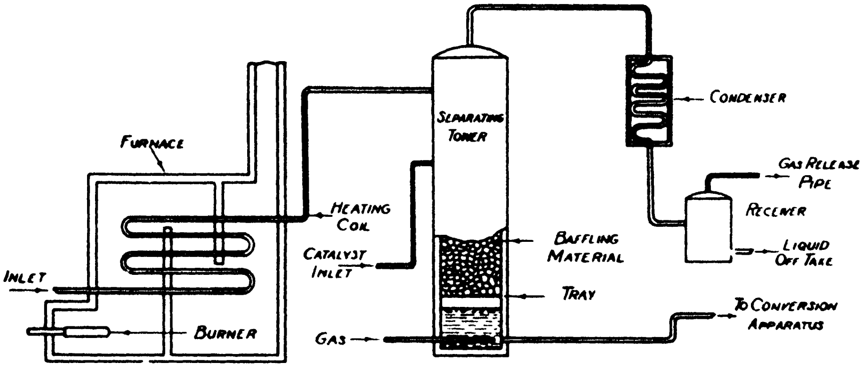

FIG. 62.—Sketch of Catalytic Cracking Process Involving Preliminary Removal of Corrosive Vapors. (W. M. Stratford)

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[7] H. Engel and J. Jannek, U. S. P. 1,941,884, Jan. 2, 1934; *J. Inst. Pet. Tech.*, 1934, **20**, 189A; *Chem. Abs.*, 1934, **28**, 1850.

[8] A. M. McAfee, U. S. P. 1,976,507, Oct. 9, 1934, to Gulf Refining Co.; *Brit. Chem. Abs.* **B**, 1935, 838; *Chem. Abs.*, 1934, **28**, 7518.

[9] V. N. Jenkins and W. M. Stratford, U. S. P. 1,953,612, April 3, 1934, to Texas Co.; *Chem. Abs.*, 1934, **28**, 3886; *Brit. Chem. Abs.* **B**, 1935, 90.

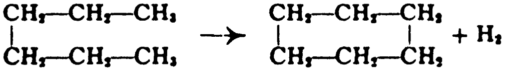
[10] W. M. Stratford, U. S. P. 1,952,898, March 27, 1934, to Texas Co.; *Chem. Abs.*, 1934, **28**, 3886; *Brit. Chem. Abs.* **B**, 1935, 90.

Carl.[11] This consists of a still fitted with a series of beaters so mounted that adjacent pairs inter-rotate in opposite directions, and thus furnish more intimate contact between the oil and catalyst.

Lelgemann[12] suggests cracking high boiling hydrocarbons at temperatures up to 370°C. in contact with 5 to 10 per cent of aluminum chloride, which is continuously reactivated by introducing charging stock containing about 0.3 per cent by weight of nitrosyl chloride. He also points out that both aluminum and iron halides may be employed in an amount not exceeding 12 per cent of the charge.[13]

ACTION OF ALUMINUM CHLORIDE ON PARAFFIN HYDROCARBONS

The action of aluminum chloride on the paraffin hydrocarbons is complex. Several different types of reaction occur simultaneously: In addition to isomerization, rupture of the carbon chain takes place with the production of a lower paraffin hydrocarbon and an unsaturated hydrocarbon fragment which is polymerized by, and probably combined with, the halide. Nenitzescu and Dragan[14] reported that freshly sublimed aluminum chloride caused *n*-hexane, at its boiling point, to partially decompose, forming a lower-boiling isomer, probably 2- or 3-methylpentane. In addition, simultaneous hydrogenation and dehydrogenation take place, producing pentane and cyclohexane in accordance with the following scheme:



$$\begin{array}{l} CH_2{-}CH_2{-}CH_3 \\ | \\ CH_2{-}CH_2{-}CH_3 \end{array} \longrightarrow \begin{array}{l} CH_2{-}CH_2{-}CH_2 \\ |\qquad\qquad\quad | \\ CH_2{-}CH_2{-}CH_2 \end{array} + H_2$$

With *n*-heptane this catalyst causes the formation of fractions boiling both lower and higher than heptane. The low boiling fractions are apparently paraffins formed by splitting of the hydrocarbon chain, while the high boiling fractions consist of mono- and bicyclic naphthenes. Moist aluminum chloride yields a considerably increased quantity of gases (cleavage products), the proportion of the latter being to some extent determined by the amount of water present. A hydrogenation action of aluminum chloride is strongly evidenced with alkyl chlorides. Under these conditions a vigorous action occurs by which the alkyl chloride is reduced to the corresponding hydrocarbon at the expense of hydrogen from the heptane, which in turn is largely converted to higher boiling cycloparaffins, and only slightly to the lower paraffins.

A similar investigation with *n*-hexane was made by Calingaert and Beatty,[15] who modified the procedure in that the low-boiling reaction products were continuously withdrawn and subsequently identified. Tarry polymerization products were also separated but not studied in detail. The yields of the various hydrocarbons isolated are given (on a percentage basis) in Table 46.

It is suggested that branched-chain heptanes may result from condensation of lower-boiling hydrocarbons formed in the reaction. *n*-Heptane refluxed with aluminum chloride yielded three hexanes, together with at least three and probably five of the eight branched-chain heptanes, these hydrocarbons totaling about 5 to 6 per cent of the reacted *n*-heptane.

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[11] B. E. Carl, U. S. P. 1,963,259, July 19, 1934, one third to C. G. Campbell; *J. Inst. Pet. Tech.*, 1934, 20, 501A; *Chem. Abs.*, 1934, 28, 5224.

[12] W. Lelgemann, U. S. P. 1,936,539, Nov. 21, 1933, one-half to H. T. Sorg; *Brit. Chem. Abs. B*, 1934, 790; *Chem. Abs.*, 1934, 28, 888.

[13] W. Lelgemann, U. S. P. 1,936,633, Nov. 28, 1933; *J. Inst. Pet. Tech.*, 1934, 20, 38A; *Chem. Abs.*, 1934, 28, 1517. See also Chapter 3.

[14] C. D. Nenitzescu and A. Dragan, *Ber.*, 1933, 66, 1892; *Chem. Abs.*, 1934, 28, 1025; *Brit. Chem. Abs. A*, 1934, 167.

[15] G. Calingaert and H. A. Beatty, *J.A.C.S.*, 1936, 58, 51; *Chem. Abs.*, 1936, 30, 1733. See also G. Calingaert and D. T. Flood, *J.A.C.S.*, 1935, 57, 956; *Chem. Abs.*, 1935, 29, 4325; *Brit. Chem. Abs. A*, 1935, 843.

TABLE 46.—*Products of Reaction of Aluminum Chloride on n-Heptane*

Hydrocarbon	% Yield
Pentanes and below	64.6
2-Methylpentane	3.4
3-Methylpentane	2.0
n-Hexane	0.4
2,4-Dimethylpentane	1.5
2,2,3-Trimethylbutane	0.5
3,3-Dimethylpentane	0.4
2-Methylhexane	1.2
3-Methylhexane	1.6
Polymerization products	24.4

Moldavskii, Kobuil'skaja and Livschitz[16] report that *n*-hexane and *n*-octane when treated with aluminum chloride at 20-90°C. gave a 30 per cent yield of isohexane and isooctane, respectively. The reaction was greatly accelerated by hydrogen chloride.

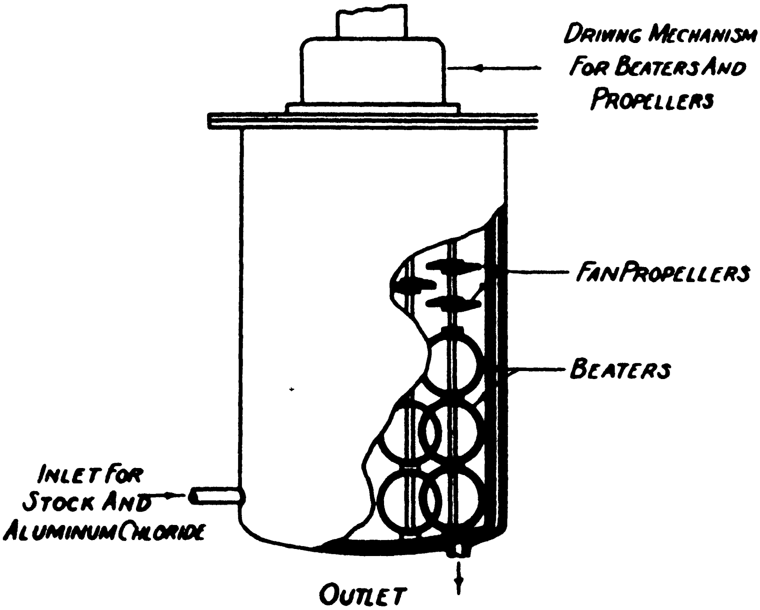
Driving Mechanism For Beaters And Propellers
Fan Propellers
Beaters
Inlet For Stock And Aluminum Chloride
Outlet

FIG. 63.—Drawing of Apparatus for Treating Petroleum Oils with Aluminum Chloride. (B. E. Carl)

The work of Grosse and Ipatieff[17] on the reaction between paraffins and aromatic hydrocarbons in the presence of anhydrous inorganic halides would seem to shed considerable light on the mechanism of the decomposition of paraffin hydrocarbons under the influence of such catalysts. By passing dry hydrogen chloride through a mixture of benzene, 2,2,4-trimethylpentane and aluminum chloride at

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[16] B. L. Moldavskii, M. V. Kobuil'skaja and S. E. Livschitz, *J. Gen. Chem.* (*U.S.S.R.*), 1935, 5, 1791; *Brit. Chem. Abs.* B, 1936, 701; *Chem. Abs.*, 1936, 30, 3402.

[17] A. V. Grosse and V. N. Ipatieff, *J.A.C.S.*, 1935, 57, 2415; *Chem. Abs.*, 1936, 30, 1751; *J. Inst. Pet. Tech.*, 1936, 22, 86A.

25 to 50°C. (or zirconium tetrachloride at 50 to 75°C.), these investigators obtained isobutane and a mixture of mono- and dibutylbenzenes. No reaction occurred in the presence of magnesium chloride or of nickel-promoted boron trifluoride. It is reasonable to assume, therefore, that aluminum chloride and zirconium tetrachloride decompose paraffins with the production of a lower paraffin and the complementary olefin, which, in the presence of aromatic hydrocarbons, is immediately converted into an alkylated aromatic hydrocarbon.

As a result of investigations involving the action of aluminum chloride on *n*-butane, *n*-hexane, *n*-heptane and 2,2,4-trimethylpentane in the presence of dry hydrogen chloride, Ipatieff and Grosse[18] proposed the following general mechanism of the reaction, which they termed an "auto-destructive alkylation." The initial reaction was considered to result in the rupture of a carbon-carbon bond and the formation of a paraffin and an olefin, either directly or through free radicals, according to the equation:

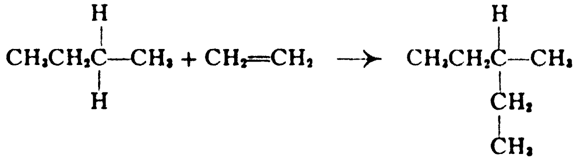
$$C_nH_{2n+2} \longrightarrow \underset{\textit{lower paraffin}}{C_{n-x}H_{2(n-x)+2}} + \underset{\textit{olefin}}{C_xH_{2x}} \qquad (1)$$

The olefin from reaction (1) can directly combine with a paraffin under the influence of a Friedel-Crafts catalyst giving a higher paraffin by alkylation.

$$C_nH_{2n+2} + C_xH_{2x} \longrightarrow \underset{\textit{higher paraffin}}{C_{n+x}H_{2(n+x)+2}} \qquad (2)$$

This is the antithesis of reaction (1) and probably accounts for the isomerization of paraffin hydrocarbons under the influence of these catalysts. Thus, the isomerization of *n*-hexane can be formulated in the following manner:

$$\underset{\textit{n-hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3} \longrightarrow \underset{\textit{n-butane}}{CH_3CH_2CH_2CH_3} + \underset{\textit{ethylene}}{CH_2{=}CH_2}$$



$$CH_3CH_2\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}{-}CH_3 + CH_2{=}CH_2 \longrightarrow CH_3CH_2\overset{H}{\underset{\substack{|\\ CH_2\\ |\\ CH_3}}{\overset{|}{C}}}{-}CH_3$$

n-butane *ethylene* *isohexane*

The olefin resulting from the first reaction may, instead of combining with a paraffin molecule, undergo polymerization to yield a higher olefin which can in turn react either with a paraffin molecule to yield a higher paraffin or with the metallic halide to form a complex (lower layer).[19]

The overall effect of the action of aluminum chloride on the paraffins is embraced in the following general equation:

$$zC_nH_{2n+2} \longrightarrow aC_{x_1}H_{2x_1+2} + bC_{x_2}H_{2x_2+2} + cC_{x_3}H_{2x_3+2} + \dots\dots \qquad (3)$$

$$\text{where } z{\cdot}n = ax_1 + bx_2 + cx_3 + \dots\dots$$

Ipatieff and Grosse found that the presence of dry hydrogen chloride was essential and in the absence of the latter no reaction took place between the Friedel-Crafts agent and paraffins except at higher temperatures (about 150-200°C.). In the case of *n*-butane, no appreciable action took place below 100°C. even in the presence of hydrogen chloride. However, at 175°C. *n*-butane was converted into propane, ethane and methane and also partly isomerized to isobutane. Treatment of *n*-hexane for 3 hours at its boiling point with aluminum chloride and a small amount of hydrogen chloride converted this hydrocarbon (to the extent of 20 to 25 per cent) into a mixture of higher- and lower-boiling paraffins including isobutane and isomeric hexanes. Decomposition of the resultant sludge with water yielded an unsaturated oil. In a similar way, *n*-heptane at its boiling point furnished, after 3 hours, about 35 to 40 per cent of paraffin hydrocarbons consisting of substances of both lower and higher boiling points than the original hydrocarbon, and unsaturated oils recovered from the sludge. In the case of 2,2,4-trimethylpentane, the reaction with the catalyst in the presence of a trace of hydrogen chloride took place even at room temperature, and after 3 to 4 hours at 25-50°C. about 90 per cent of this octane was converted into lower and higher boiling paraffin hydrocarbons. In addition, a small amount of unsaturated oil was recovered by decomposing the aluminum chloride sludge with water. Of special interest in this work was the production of relatively large amounts of isobutane from the various paraffin hydrocarbons.

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[18] V. N. Ipatieff and A. V. Grosse, *Ind. Eng. Chem.*, 1936, **28**, 461; *Chem. Abs.*, 1936, **30**, 3410.

[19] See also V. N. Ipatieff, A. V. Grosse, H. Pines and V. I. Komarewsky, *J.A.C.S.*, 1936, **58**, 913; *Chem. Abs.*, 1936, **30**, 5173; *Brit. Chem. Abs.* **A**, 1936, 960; *J. Inst. Pet. Tech.*, 1936, **22**, 394A. Also V. N. Ipatieff and A. V. Grosse, *J. Gen. Chem.* (*U.S.S.R.*), 1936, **6**, 423; *Brit. Chem. Abs.* **A**, 1936, 960.

Glasebrook, Phillips and Lovell[20] obtained analogous results with aluminum chloride and *n*-pentane. These investigators also noticed that this promoter did not react detectably in completely anhydrous media, even over considerable periods. Addition of small amounts of water, hydrated aluminum chloride, or alkyl chlorides initiated disintegration. However, when aluminum oxide was added to an anhydrous aluminum chloride-*n*-pentane mixture, no reaction resulted, thus indicating that hydrogen chloride was the activating substance. (Hydrogen bromide served equally well in this capacity.) The principal products of the decomposition are isopentane and butanes, the quantity of the latter increasing linearly with reaction time. The isopentane concentration, however, increases rapidly toward a maximum value, then declines slowly with continued contact. Certain undefined, saturated high-boiling products and an insoluble, unsaturated polymer were also isolated but were not identified.

These workers found that aluminum bromide, on the other hand, although giving rise to the same products, did not require the addition of an initiating agent, and even under anhydrous conditions reacted readily and considerably more vigorously than did the chloride. A reaction mixture containing 1.52 mole per cent of aluminum bromide dissolved in the pentane underwent the same conversion in one half the time as did a mixture containing 17.4 mole per cent of aluminum chloride (promoted by 0.2 per cent of water per mole of aluminum chloride).

The decomposition of octadecane and hexatriacontane by anhydrous aluminum chloride has been discussed by Bauer and Toma.[21] The light liquid products boiling up to 175°C. appeared to be entirely saturated and probably paraffinic, since they were not attacked by strong sulphuric acid and had iodine numbers of practically zero. Octadecane yielded 60 per cent of liquids boiling up to 175°C., 13 per cent of a gas (85 per cent of which was lower paraffins), and a residue of carbonaceous material. Under similar conditions hexatriacontane furnished 33 per

[20] A. L. Glasebrook, N. E. Phillips and W. G. Lovell, *J.A.C.S.*, 1936, 58, 1944; *Chem. Abs.*, 1936, 30, 8145; *J. Inst. Pet. Tech.*, 1937, 23, 22A; *Brit. Chem. Abs.* A, 1936, 1485.

[21] K. H. Bauer and V. Toma, *Ber.*, 1934, 67, 1135; *Chem. Abs.*, 1934, 28, 5804; *Brit. Chem. Abs.* A, 1934, 864.

cent of volatile liquids, 30 per cent of heavy oils boiling up to above 450°C., 24 per cent of carbonaceous residue and 13 per cent of gas.[22]

It appears from the work of Petrov, Meshcheryakov and Andreev[23] that anhydrous zinc chloride, though much less active than aluminum chloride, is capable of causing the isomerization of paraffins at fairly high temperatures. Thus, with this chloride, *n*-heptane was found to isomerize to the extent of 20 to 25 per cent in 6 hours at 300 to 400°C. under 50 atmospheres of hydrogen.

ACTION OF ALUMINUM CHLORIDE ON UNSATURATED HYDROCARBONS

The mechanism of the vigorous action between Friedel-Crafts agents and olefins has not yet been elucidated. Polymerization is perhaps the most important reaction, especially at low temperatures, but other transformations, such as isomerization and splitting off of lower paraffin hydrocarbons, also take place. In general the products obtained from olefins at low temperatures consist of a polymerized free oil and a metal halide-hydrocarbon complex, from which the combined oil can be liberated by decomposition with water. At higher temperatures the free oil invariably contains large proportions of paraffin hydrocarbons in the lower boiling fractions, and the metal-hydrocarbon complex tends to coke.

The polymerization of ethylene by means of a suspension of aluminum chloride in pentane at 125 to 150°C. and under a pressure of 70 to 250 kilograms per sq. cm. has been examined by Waterman and Tulleners.[24] The combined oil, representing about 10 per cent of the total oil yield, was liberated from the pasty complex and separated into fractions, each of which was subjected to hydrogenation. From the results it was concluded that this oil is highly unsaturated and contains cyclic hydrocarbons, the average number of rings per molecule increasing from 1.2 in the lower boiling fractions to 2.5 in the viscous higher fractions. The free oil consisted almost entirely of paraffin hydrocarbons (especially in the lighter fractions), with an increasing proportion of saturated cyclic hydrocarbons in the high-boiling portions.

From the physical properties of the lower boiling substances Waterman and Tulleners deemed it probable that considerable proportions of branched-chain paraffins were present. This is supported by the work of Bowen and Nash,[25] who examined the liquid boiling up to 200°C. (51 per cent by volume of the crude product) formed by polymerizing ethylene with aluminum chloride at 150 to 160°C. under a pressure of 45 to 55 atmospheres. The octane number of this ethylene-polymer liquid averaged about 77 and was thus considerably higher than a Pennsylvania straight-run motor fuel. This fact in conjunction with other physical characteristics indicated the presence of large proportions of branched-chain paraffins.

In view of the experiments involving paraffins and olefins, Ipatieff and Grosse[26] believe that reactions using low-boiling paraffins as "inert solvents" might not give a true picture of the condensation of ethylene alone. Studies were therefore carried out using pure ethylene and pure aluminum chloride in glass-lined autoclaves. These workers also point out that the pure, dry substances do not react, even under pressures up to 50 atmospheres at 10° to 50°C., but that traces of hydrogen chloride (or moisture) must be present. Under the latter conditions, a maximum of about 10 molecules of ethylene are condensed by 1 molecule of the catalyst (thus 100 grams of catalyst polymerized 193 grams of ethylene). Investigation of the polymer resulting from treatment of ethylene at 25° to 30°C. under 20 atmospheres pressure showed considerable chemical difference between the free upper layer and the combined lower layer. The former was almost wholly paraffinic, though the reactivity toward potassium permanganate solution indicated the presence of some unsaturates and possibly naphthenes. The lower layer, however, after decomposition with ice water, was completely soluble in 96 per cent sulphuric acid, suggesting that it was entirely composed of unsaturates. Molecular weight and bromine number determinations gave an average value of two to three double bonds per molecule. Hydrogenation of certain fractions (boiling between 175° and 212°C. and 264° to 292°C.) yielded naphthenes, and hence, the original fractions were considered to have been cyclic unsaturated hydrocarbons of the terpene type. The polymerization mechanism was believed to begin as follows:

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[22] H. Gault and R. Sigwalt (*Ann. combustibles liquides*, 1927, **2**, 309, 543; *Chem. Abs.*, 1928, **22**, 379) obtained chiefly butane and a little propane in the gaseous products of the cracking of hexadecane in the liquid phase in the presence of aluminum chloride.

[23] A. D. Petrov, A. P. Meshcheriakov and D. N. Andreev, *Ber.*, 1935, **68**, 1; *Chem. Abs.*, 1935, **29**, 2145; *Brit. Chem. Abs.* **A**, 1935, 324.

[24] H. I. Waterman and A. J. Tulleners, *Chim. et ind.*, 1933, **29**, 496; *Chem. Abs.*, 1933, **27**, 5715; *Brit. Chem. Abs.* **B**, 1934, 135.

[25] A. R. Bowen and A. W. Nash, *World Petroleum Congress*, 1933, **2**, 774; *Chem. Abs.*, 1934, **28**, 4871; *Brit. Chem. Abs.* **B**, 1934, 744.

[26] V. N. Ipatieff and A. V. Grosse, *J.A.C.S.*, 1936, **58**, 915; *Brit. Chem. Abs.* **A**, 1936, 960; *Chem. Abs.*, 1936, **30**, 5175.

$$H_2C{=}CH_2 + HCl \xrightarrow{(AlCl_3)} H_3CCH_2Cl$$

$$H_3CCH_2Cl + H_2C{=}CH_2 \xrightarrow{(AlCl_3)} CH_3CH_2CH{=}CH_2 + HCl$$

Polymerization of a mixture of lower gaseous olefins (85 per cent total unsaturates) by aluminum chloride has been studied by Potolovskii and Atal'yan.[27] The products obtained at room temperature after ten days contained 45 to 50 per cent of gasoline and kerosene hydrocarbons and 50 to 55 per cent of heavier oil. The latter had a lower specific gravity and a higher viscosity index than corresponding natural oil fractions. The residue obtained on vacuum distillation was a drying oil formed by the polymerization of diolefins with olefins and to some extent with benzene. When polymerization was carried out at 70°C., the resulting hydrocarbons had a lower average boiling point.

The preparation of gasoline from unsaturated hydrocarbon gases by passage at 350° to 700°F. and 600 to 1500 lbs. per sq. in. pressure over catalysts of the metallic halide type, including also iron chloride and titanium chloride, has been described by Wagner.[28]

The lower olefins having a branched-chain structure, such as isobutene and trimethylethylene, are particularly susceptible to polymerization under the influence of Friedel-Crafts condensing agents. The former reacts violently even at temperatures as low as −80°C. and the products have a very high mean molecular weight. According to Waterman, Over and Tulleners,[29] such low temperature polymers have a partly cyclic structure and are mainly saturated. High molecular weight substances having a more or less cyclic character have also been obtained by polymerization of isopropylethylene, *asym*-methylethylethylene and trimethylethylene by aluminum chloride at −80°C.[30] At higher temperatures (85° and 200°C.) yields of substances having partly cyclic structures (i.e., naphthenic hydrocarbons) have been obtained.[31] Iso-olefins have been reacted at temperatures as low as —80°C. with catalysts such as boron trifluoride.[32] Thus the action of gaseous or solid volatile halides of elements of Groups 2, 5, 6 and 8 (e.g. beryllium, arsenic, uranium, iron or osmium chlorides or fluorides) on liquid isobutene at temperatures above —10°C. produces high molecular weight polymers. The liquid volatile halides such as tin tetrachloride, titanium tetrachloride or antimony pentafluoride may also be used, as well as aluminum chloride (formed *in situ* by the action of hydrogen chloride on aluminum chips, previously activated with mercuric chloride) at temperatures not above 50°C.[33]

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[27] L. Potolovskii and A. Atal'yan, *Azer. Neft. Khoz.*, 1935, 1, 109; *Chem. Abs.*, 1935, **29**, 6032.

[28] C. R. Wagner, U. S. P. 1,934,896, Nov. 14, 1933, to Pure Oil Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 40A; *Chem. Abs.*, 1934, **28**, 631.

[29] H. I. Waterman, J. Over and A. J. Tulleners, *Rec. trav. chim.*, 1934, **53**, 699; *Chem. Abs.*, 1934, **28**, 5397; *Brit. Chem. Abs.* A, 1934, 864.

[30] J. J. Leendertse, A. J. Tulleners and H. I. Waterman, *Rec. trav. chim.*, 1934, **53**, 715; *Chem. Abs.*, 1934, **28**, 5398; *Brit. Chem. Abs.* A, 1934, 864.

The straight-chain olefins do not react as vigorously as the branched isomers. Polymerization of pentene-2 with aluminum chloride as a catalyst is slow at —80°C. but more rapid at 0°C. From pentene-2 and this catalyst at 0°C. Waterman, Leendertse and Klazinga[34] obtained a free oil (constituting about 80 per cent of the total reaction resultants) which had very low bromine absorption values and appeared to be a mixture of aliphatic and naphthenic hydrocarbons.

No appreciable reaction of cyclohexene with aluminum chloride has been found by Waterman, Leendertse and ter Poorten[35] at temperatures below 0°C., and even at 40°C. polymerization was still very slow. However, it was possible to condense cyclohexene quite rapidly at 70°C. to high molecular weight polymers. Approximately equal proportions of free and combined oils resulted. The latter liberated from the complex, was more unsaturated than the free oil, which had a very low bromine number. Hydrogenated fractions of both the free and combined oils had specific refractivities in close agreement with those calculated for cyclohexyl hydrocarbons of the same molecular weight. In the presence of hydrogen chloride, however, cyclohexene was found to react vigorously under the influence of aluminum chloride catalysis even at —78°C. to furnish a mixture of monochlorocyclohexane and monochloropolycyclohexyl compounds, the latter being formed by the addition of hydrogen chloride to the cyclohexene polymers.

Action of Aluminum Chloride on Cycloparaffins

The action of aluminum chloride on cyclohexane, alone or in the presence of other substances, has received considerable study. In order to explain the reaction between this hydrocarbon and acetyl chloride in the presence of Friedel-Crafts agents, Zelinskii and Tarasova[36] considered that the initial change was one of dehydrogenation in which cyclohexane behaves as a mixture of *cis*- and *trans*-isomers. The *cis*-form furnishes cyclohexene (converted to tetrahydroacetophenone by acetyl chloride) while dehydrogenation of the *trans*-form was thought to proceed through a dicyclic system, which could undergo fission to yield unsaturated radicals, as summarized below:

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[31] H. I. Waterman, J. J. Leendertse and W. M. Klazinga, *Rec. trav. chim.*, 1935, **54**, 79; *Chem. Abs.*, 1935, **29**, 2503. The polymers from pentene-2 have also been described by H. I. Waterman and J. J. Leendertse, *Rec. trav. chim.*, 1935, **54**, 139; *J. Inst. Pet. Tech.*, 1935, 21, 371A; *Chem. Abs.*, 1935, **29**, 2803. See also the description of the physical properties of the polymers of the branched pentenes given by H. I. Waterman, J. J. Leendertse and J. P. Makkink, *J. Inst. Pet. Tech.* 1936, **22**, 333, 298A; *Chem. Abs.*, 1936, **30**, 5773.

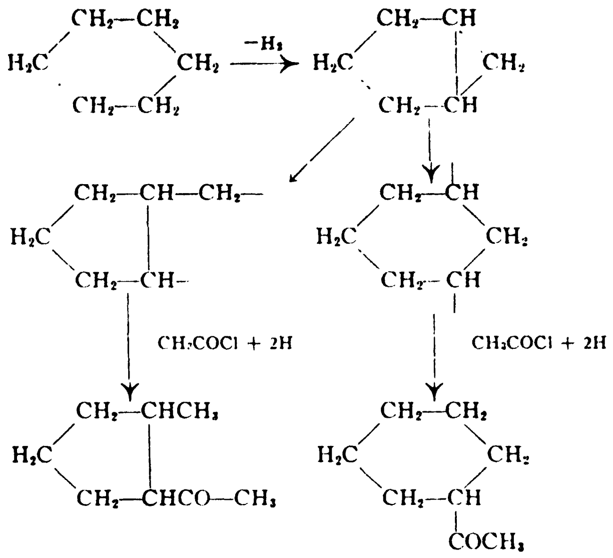
[32] British P. 401,297, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 2367; *Brit. Chem. Abs.* B, 1934, 136.

[33] British P. 421,118, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 3353; *Brit. Chem. Abs.* B, 1935, 182.

[34] H. I. Waterman, J. J. Leendertse and W. M. Klazinga, *loc. cit.*

[35] H. I. Waterman, J. J. Leendertse and A. C. ter Poorten, *Rec. trav. chim.*, 1935, **54**, 245; *Chem. Abs.*, 1935, **29**, 2803; *Brit. Chem. Abs.* A, 1935, 480.

[36] N. D. Zelinskii and E. M. Tarasova, *Ann.*, 1934, **508**, 115; *Chem. Abs.*, 1934, **28**, 3384; *Brit. Chem. Abs.* A, 1934, 295.



The two ketones produced, namely cyclohexyl methylketone and 2-acetyl-1-methylcyclopentane, were considered to be derived from the two unsaturated residues by direct combination of acetyl chloride and hydrogen with elimination of hydrogen chloride. To account for the production of 1-methyl-2-acetylcyclopentane from cyclohexane and acetyl chloride in the presence of aluminum chloride, Nenitzescu and Cantuniari[37] assumed that cyclohexane is first isomerized to methylcyclopentane, which then undergoes dehydrogenation to methylcyclopentene, the latter subsequently reacting with acetyl chloride. Later, Nenitzescu and Isacescu[38] found that, in the absence of a hydrogen acceptor, the main reaction between aluminum chloride and cyclohexane was isomerization to methylcyclopentane. With substances readily reducible by hydrogen (such as arsenic, antimony, or phosphorus trichloride, sulphur chlorides and sulphuryl chloride), the predominant effect was a dehydrogenating condensation, which occurred according to the equations:

$$2C_6H_{12} \longrightarrow C_{12}H_{22} + H_2$$
$$3C_6H_{12} \longrightarrow C_{18}H_{32} + 2H_2$$

Thus, by the action of aluminum chloride and arsenic trichloride on cyclohexane at 65-70°C., the hydrocarbon $C_{12}H_{22}$, melting at 46°C., was produced.

The action of aluminum chloride on cyclohexane in the presence of hydrogen chloride at a temperature of 150°C. has been investigated by Ipatieff and Komarewsky,[39] and under these conditions the hydrocarbon suffered profound change. The resultant consisted of a small percentage of gas, containing a large proportion of isobutane, and a mixture of liquid hydrocarbons in which methylcyclopentane, 1,3-dimethylcyclohexane, dimethyldicyclopentyl (melting at 46-47°C. and identical with the $C_{12}H_{22}$ hydrocarbon obtained by Nenitzescu and his collaborators) and dicyclohexyl. Ipatieff and Komarewsky believed that dimethylcyclohexane was formed by isomerization of ethylcyclohexane. The latter resulted from ethylation of cyclohexane by ethylene (a decomposition product of the original hydrocarbon). The $C_{12}H_{22}$ hydrocarbons were probably formed by dehydrogenation and condensation, and the lower paraffins by destructive hydrogenation. The whole reaction scheme may be written:

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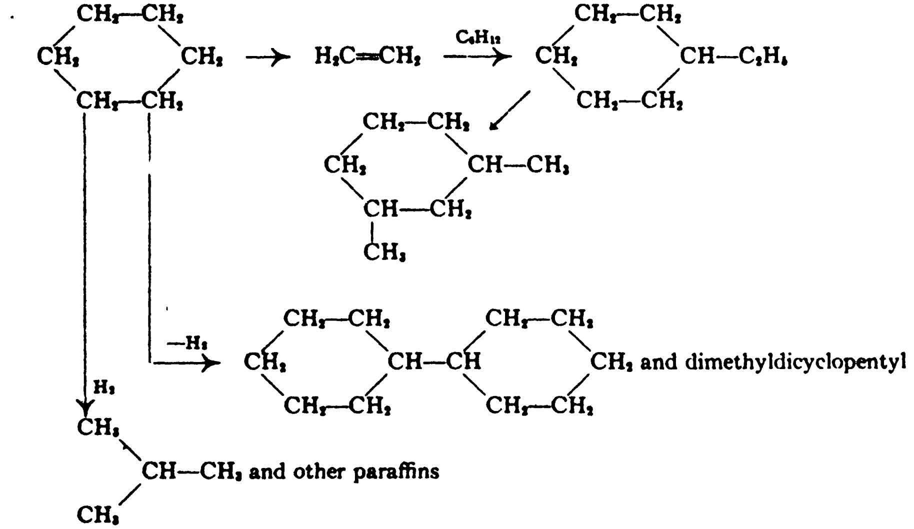
[37] C. D. Nenitzescu and I. P. Cantuniari, *Ann.*, 1934, 510, 269; *Chem. Abs.*, 1934, 28, 5413; *Brit. Chem. Abs.* A, 1934, 773.

[38] C. D. Nenitzescu and D. A. Isacescu, *Ber.*, 1934, 67, 1391; *Chem. Abs.*, 1934, 28, 7252; *Brit. Chem. Abs.* A, 1934, 995.

[39] V. N. Ipatieff and V. I. Komarewsky, *J.A.C.S.*, 1934, 56, 1926; *Chem. Abs.*, 1934, 28, 6704; *Brit. Chem. Abs.* A, 1935, 1209.



From a study of the decomposition of a number of simple cyclohexane hydrocarbons by heating at 120 to 130°C. with 10 per cent finely ground aluminum chloride, Turova-Polyak[40] has concluded that these monocyclic compounds can be isomerized to cyclopentane rings. Thus, under the conditions stated above methylcyclohexane gave rise to cyclohexanes, cyclopentanes and paraffins in the ratio 78.6:20.4:1.0 respectively. Under similar treatment dimethylcyclohexane yielded fractions in which the percentages of cyclohexanes varied from 84.6 to 68.9, the cyclopentanes from 19.4 to 11.5 per cent, and the paraffins from 11.7 to 4.0 per cent. Aluminum chloride also was found to cause isomerization of ethylcyclohexane to 1,3-dimethylcyclohexane.

By decomposition of decahydronaphthalene with 10 per cent of aluminum chloride at 175 to 210°C., Zelinskii and Turova-Polyak[41] obtained a mixture of liquid hydrocarbons boiling between 80 and 180°C. but practically no gas was evolved. In this instance the reaction product consisted almost entirely of cyclohexane and cyclopentane hydrocarbons and dicyclic hydrocarbons of the type of dimethyldicyclopentane, with only small amounts of paraffins. It was concluded that the *cis*-form of decalin was first isomerized to the *trans*-isomer, which in turn was converted into dimethyldicyclopentyl.

ACTION OF ALUMINUM CHLORIDE ON AROMATIC HYDROCARBONS

In the products of the action of aluminum chloride on benzene, several hydrocarbons have been identified, including biphenyl, toluene and ethylbenzene.[42] Gustavson[43] obtained 1-methyl-3-phenylcyclopentane and diphenylcyclohexane by treating benzene in this manner at room temperature for several weeks. Later, Wertyporoch and Sagel[44] secured phenylcyclohexane, biphenyl, *o*-diphenylcyclohexane and a mixture of phenylated methylcyclopentanes and cyclohexanes by the prolonged action of aluminum bromide on benzene at 18°C. In addition, phenolic substances were also formed, probably as the result of the intervention of oxygen or water. By heating benzene at 125°C., in an autoclave (in the absence of air), with 10 per cent of aluminum chloride and small amounts of dry hydrogen chloride, Ipatieff and Komarewsky[45] obtained 1.7 per cent of ethylbenzene and 0.8 per cent of biphenyl, calculated on the benzene charged. The presence of ethylbenzene was thought to be due to the direct ethylation of benzene by ethylene released by destructive hydrogenation of the benzene. This mechanism was supported by the fact that unsaturated polymers of ethylene were recovered from the sludge.

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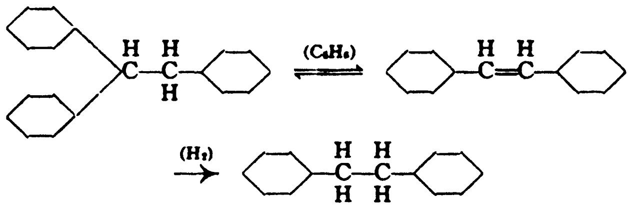
[40] M. B. Turova-Polyak, *Ber.*, 1935, 68, 1781; *Chem. Abs.*, 1935, 29, 7951; *Brit. Chem. Abs.* A, 1935, 1358.

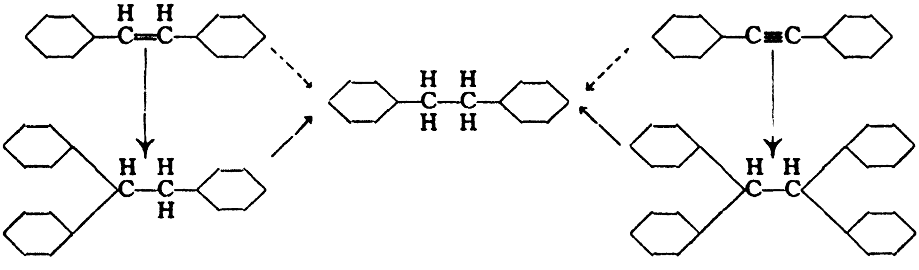
[41] N. D. Zelinskii and M. B. Turova-Polyak, *J. Appl. Chem.* (*U.S.S.R.*), 1934, 7, 753; *Chem. Abs.*, 1935, 29, 2528; *Brit. Chem. Abs.* A, 1935, 204.

[42] In the presence of aluminum chloride, the exchange reaction between hydrogen and "heavy hydrogen," or deuterium, in benzene proceeds almost quantitatively, A. Klit and A. Langseth (*Z. physik. Chem.*, 1936, A176, 65; *Chem. Abs.*, 1936, 30, 5091; *Brit. Chem. Abs.* A, 1936, 714) have reported.

Alexander and Fuson[46] observed that ethylenic bonds between phenyl groups, as in stilbene, are hydrogenated in the presence of aluminum chloride and benzene. It is believed that phenylation (i.e., to produce triphenylethane) competes with hydrogenation (leading to the formation of bibenzyl). The reaction producing bibenzyl is, however, irreversible, while that yielding triphenylethane is reversible:



Thus, the production of bibenzyl in the presence of benzene and aluminum chloride is a general phenomenon for the acetylene and ethylene derivatives which bear one or more phenyl groups on each carbon atom. This general statement is represented in the following schematic reaction:



A product containing up to 98 per cent of the theoretical amount of deuterium was prepared by the interaction of deuterium chloride and benzene in the presence of the catalyst. The properties compare with those of hydrogen benzene as follows:

Benzene	Density	Melting Point °C.
C_6H_6	0.878	5.5
C_6D_6	0.9483	6.64

When exchange of hydrogen and deuterium takes place, the deuterium atoms are distributed between the benzene nuclei in such a way that the product is a mixture of the possible isomeric deuteriobenzenes in such proportions as correspond with the laws of probability.

[43] G. Gustavson, *Compt. rend.*, 1908, 146, 640; *Chem. Abs.*, 1908, 2, 1698.

[44] E. Wertyporoch and H. Sagel, *Ber.*, 1933, 66, 1306; *Chem. Abs.*, 1934, 28, 116; *Brit. Chem. Abs.* A, 1933, 1152.

[45] V. N. Ipatieff and V. I. Komarewsky, *J.A.C.S.*, 1934, 56, 1926; *Chem. Abs.*, 1934, 28, 6704; *Brit. Chem. Abs.* A, 1935, 1209.

[46] L. L. Alexander and R. G. Fuson, *J.A.C.S.*, 1936, 58, 1745; *Chem. Abs.*, 1936, 30, 7549.

Rearrangement and fission of side chains appears to be the predominating result of the action of the metal halide on the alkylbenzenes, although some dehydrogenation combined with condensation also takes place. Benzene, methylcyclohexane, *m*- and *p*-xylene, ethylbenzene, ditolyl and dimethylanthracene have been isolated from the products of the action of aluminum chloride on toluene at the boiling point.[47] From xylenes and the same catalyst benzene, toluene, pseudocumene, mesitylene and durene were recovered.[48] Isomerization of *o*- and *p*-xylenes to *m*-xylene at 100°C. was noticed by Heise and Töhl.[49] Later, Popov[50] obtained 7 per cent of benzene and 11 per cent of toluene by heating xylene at its boiling point under ordinary pressure with 2 per cent of aluminum chloride. He also noticed that the more resistant *meta*-isomer accumulated upon recycling unreacted xylene. Dealkylation of aromatic hydrocarbons by aluminum chloride has been studied by Orlov and Solodar',[51] who noted that the yield of low-boiling products increased with rising temperature and with the concentration of aluminum chloride, the optimum amount of the latter being 4 per cent. Demethylation of xylene under the influence of the halide and hydrogen chloride resulted in poor yields though a continuous process was developed whereby the production of toluene could be raised to about 25 per cent.

In a similar way, the chloride causes rearrangement of side chains in many other alkylbenzenes. Ethylbenzene is converted by it to benzene, diethylbenzene and triethylbenzene.[52] Isopropylbenzene is decomposed to furnish benzene and diisopropylbenzene, and *n*-butylbenzene is partly transformed into benzene and dibutylbenzene.[53] On the other hand, Ipatieff and Pines[54] report that alkylbenzenes react in certain solvents, such as cyclohexane and decahydronaphthalene, to yield the alkyl group as a paraffin, when in the presence of aluminum chloride. Thus, propylbenzene in cyclohexane yields propane. Decahydronaphthalene served to facilitate this reaction to a greater degree than did the cyclohexane, as the results in Table 47 indicate.

TABLE 47.—*Paraffins from Alkylbenzenes.*

Aromatic Hydrocarbon Used	Paraffin Formed	In Cyclohexane, % Yield	In Decahydronaphthalene, % Yield
Toluene	None	0	0
Ethylbenzene	None	0	0
Isopropylbenzene	Propane	33	53
sec-Butylbenzene	Butane	35	71
ter-Butylbenzene	Isobutane	61	94
2-Methyl-3-phenylbutane	Isopentane	60	..

It was pointed out that this reaction might be of considerable use in determining the structure of alkyl groups attached to an aromatic nucleus.

In the case of the polynuclear aromatic hydrocarbons under similar conditions, the main reaction observed is one of dehydrogenating condensation. In this way, naphthalene is partly changed into 2,2′-dinaphthyl, and phenanthrene undergoes internal rearrangement with loss of hydrogen to give 2,3,10,11-dibenzoperylene.[55] The conversion of 1,1′-dinaphthyl into perylene by heating with aluminum chloride at 140°C. was observed by Scholl, Seer and Weitzenböck.[56] 2,2'-Dinaphthyl is said to yield the same hydrocarbon by similar treatment at 130° to 160°C.[57]

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[47] R. J. Moore and G. Egloff, *Chem. Met. Eng.*, 1917, 17, 61; *Chem. Abs.*, 1917, 11, 2665.

[48] R. Anschütz and H. Immendorff, *Ber.*, 1885, 18, 657; L. I. Smith and O. W. Cass, *J.A.C.S.*, 1932, 54, 1603, 1609, 1614; *Chem. Abs.*, 1932, 26, 2714.

[49] R. Heise and A. Töhl, *Ann.*, 1892, 270, 155; *J.C.S.*, 1892, 62, 1309.

[50] S. N. Popov, *Azer. Neft. Khoz.*, 1934, No. 7-8, 121; *Chem. Abs.*, 1935, 29, 6034; *Brit. Chem. Abs.* B, 1936, 631.

[51] N. N. Orlov and L. S. Solodar', *J. Applied Chem. U.S.S.R.*, 1935, 8, 117; *Chem. Abs.*, 1935, 29, 7296; *Brit. Chem. Abs.* A, 1935, 967.

[52] R. Anschütz, *Ann.*, 1886, 235, 150.

[53] R. Heise and A. Töhl, *loc. cit.*

[54] V. N. Ipatieff and H. Pines, *J.A.C.S.*, 1937, 59, 56; *Chem. Abs.*, 1937, 31, 1372.

[55] E. Clar, *Ber.*, 1932, 65, 846; *Chem. Abs.*, 1932, 26, 4046.

INDUSTRIAL APPLICATIONS OF THE POLYMERIZATION OF OLEFINS BY METAL HALIDES

Polymerization of Gaseous Olefins. In countries where petroleum deposits are small, or lacking, the possibilities in polymerization of the olefins to synthetic lubricating oils have aroused considerable interest. When unsaturated hydrocarbon mixtures such as those derived from the cracking of petroleum distillates are treated with Friedel-Crafts agents, not only do polymerizations take place, but also condensation reactions combining olefins with any aromatic or naphthenic hydrocarbons present. Such reactions are more fully discussed in Chapter 24, but some consideration of them will be given in the present connection.

Petrov, Antzuz and Pozhiltzeva[58] investigated the reactions of a gas containing 20 to 33 per cent of olefins with aluminum chloride in a petroleum ether suspension, under 40 to 60 atmospheres pressure. The experiments were run first at room temperature, when a free oil and a combined sludge were formed. The former appeared to consist largely of paraffins and naphthenic hydrocarbons with long side-chains. The combined oil was freed from the aluminum chloride-hydrocarbon complex by the action of water. Distillation curves of both these oils indicated a smaller number of chemical individuals than similar fractions from natural petroleum.[59] The viscosity-temperature curves of the new materials compared favorably with the curves of American petroleum oils of similar viscosity.

At 100°C. the reaction was more rapid,[60] and the resultant substances quite different in character from those obtained by room-temperature reaction. The free oil now contained appreciable proportions of unsaturated hydrocarbons, and the quantity of combined oil was notably smaller. Moreover, the higher-temperature reaction produced lubricants characterized by steeper viscosity-temperature curves. Though benzene had not been present initially, considerable quantities of hexaethylbenzene were isolated from the reaction products.

Working with a mixture of lower paraffins and olefins (ethane, ethylene, propane, propene, butane and butene, with 72 per cent total olefins) Potolovski and Atalijan[61] obtained a product consisting of about 50 per cent gasoline and kerosene and 50 per cent oils. In this case the reaction was conducted for 10 days at room temperature. However, they found that raising the temperature of polymerization to 70°C. favored formation of lower boiling products.

Schildwächter[62] conducted some experiments condensing ethylene with various substances, such as naphthalene, tetralin and coal-tar oils, in the presence of a

[56] R. Scholl, C. Seer and R. Weitzenböck, *Ber.*, 1910, **43**, 2202; *Chem. Abs.*, 1910, **4**, 2929.

[57] F. Kuhrmann, U. S. P. 1,977,768, Oct. 23, 1934, to General Aniline Works, Inc.; *Chem. Abs.*, 1935, **29**, 182. British P. 425,363, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1935, 443; British P. 445,896, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 6767.

[58] A. D. Petrov, L. I. Antzuz and E. N. Pozhiltzeva, *J. Applied Chem.*, 1932, **5**, 790; *Chem. Abs.*, 1933, **27**, 185; *Brit. Chem. Abs.* **B**, 1933, 212.

[59] D. L. Woodhouse (*J. Inst. Pet. Tech.*, 1934, **20**, 1057; *Chem. Abs.*, 1935, **29**, 1236; *J. Inst. Pet. Tech.*, 1935, **21**, 18A) became interested in these ethylene-polymer oils during the course of some studies on the carcinogenicity of mineral oils. It had been shown that products subjected to high temperatures in the course of their preparation were more apt to have biological effects than similar material prepared by low-temperature processes. These considerations led him to test the polymer oils composed of few chemical components, arising from known sources under known conditions and at no time subjected to high temperature. Experimentation showed that these materials displayed distinctly less carcinogenic power than did certain natural petroleum oils.

[60] According to L. A. Gukhman and E. Andreeva (*Azer. Neft. Khoz.*, 1934 (7-8), 117; *Chem. Abs.*, 1935, **29**, 6036) the polymerization of cracked distillates by aluminum chloride is 7 to 10 times as rapid at 115° to 130°C. as at 50° to 60°C.

[61] L. Potolovski and A. Atalijan, *Azer. Neft. Khoz.*, 1935, **1**, 109; *Brit. Chem. Abs.* **B**, 1936, 627.

[62] H. Schildwächter, *Angew. Chem.*, 1934, **47**, 677; *Brit. Chem. Abs.* **B**, 1934, 996; *Chem. Abs.*, 1934, **28**, 328.

halide catalyst (such as aluminum chloride) under pressure. With naphthalene, at a temperature of 100° to 180°C. and 5 per cent of the catalyst, the yield contained about 85 per cent of bright lubricant which did not darken upon standing. Molecular weight determinations indicated four or more ethyl groups in the resulting naphthalenic molecules. The viscosity-temperature curves of one fraction of this ethylated naphthalene were comparable to those of Pennsylvania crude motor oils of similar viscosity. The ethylation of tetralin yielded only about 27 per cent of substances having the desired qualities, the remainder having lower viscosities and corresponding to di- and tri-ethylated tetralin. Coal tar was ethylated at temperatures between 290° and 330°C., the product (33 per cent) in this case being a good grade of lubricant, stable and free of asphalt. All the oils showed a good measure of resistance to oxidation. By means of the silent electric discharge, the viscosities could be further increased.[63]

Atkinson and Storch[64] polymerized ethylene in two steps by two methods. Thermal polymerization at 370°C. under a pressure of 70 atmospheres was followed by treatment with aluminum chloride at normal pressure. The resultants were a free oil yielding lubricant fractions under vacuum distillation, and a combined oil. This latter was liberated from the complex by decomposition with ice water and proved to be highly unsaturated and dark in color. The lubricant fraction of the free oil (about 30 per cent of the raw material) gave viscosity indices comparable with those of oils obtained by direct treatment of ethylene with a Friedel-Crafts agent.[65] From an investigation of the polymers formed in the reaction of different pentene isomers in the presence of halide catalysts, Waterman, Leendertse and Makkink[66] concluded that the degree of ramification of the starting material has little influence on the viscosity of the resultant oils. Experiments were reported in which pentene-2, trimethylethylene and *asym*-methylethylethylene polymers were studied, particularly as regards their viscosities. The polymers prepared under similar conditions exhibited very closely analogous viscosity indices and viscosity-temperature curves.

Lubricating oils have also been manufactured by treating a highly polymerized isobutene product in a hydrocarbon oil with a condensing agent such as aluminum chloride at 40 to 80°C.[67] Polymerization of isobutene may be made a selective process, Mueller-Cunradi and Otto[68] report. Thus it is possible to remove isobutene from mixtures containing other olefins, (including butenes). Boron trifluoride is the catalyst suggested in this process, though aluminum chloride, or titanium tetrachloride may also be used. The investigators state that at room temperatures, short contact times (of the order of one minute) permit polymerization of isobutene, and facilitate separation of this olefin from the mixture. Temperatures up to 100°C. may be employed, although at these higher temperatures the polymerized products tend to decompose to di- and trimeric compounds. It is said that a mixture of 1 part of isobutene and 2.5 parts of normal butene may be separated by treatment in this way with boron trifluoride at room temperature, so that less than 0.5 per cent of the isoolefin remains unaltered. The isobutene may be recovered from the oily polymer by distilling the latter over activated carbon at 300°C.

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[63] In this connection, A. D. Petrov (*Chim. Tverd. Topl.*, 1934, **5**, 632; *Brit. Chem. Abs.* **B**, 1936, 52) has shown that the action of the silent electric discharge differs from that of aluminum chloride in that the former polymerizes paraffins, naphthenes and aromatics as well as olefins. See also Chapter 9.

[64] R. G. Atkinson and H. H. Storch, *Ind. Eng. Chem.*, 1934, **26**, 1120; *Chem. Abs.*, 1934, **28**, 7508; *Brit. Chem. Abs.* **B**, 1935, 889.

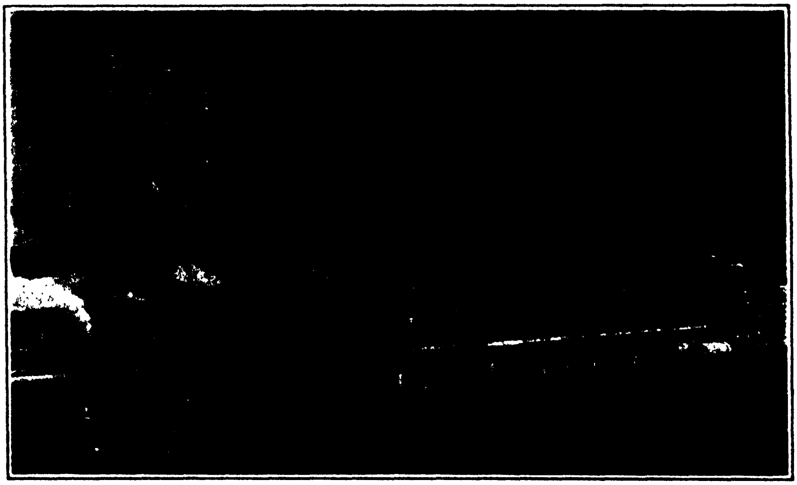
[65] *Cf.* German P. 624,583, 1936, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1936, **30**, 5027.

[66] H. I. Waterman, J. J. Leendertse and J. P. Makkink, *J. Inst. Pet. Tech.*, 1936, **22**, 333; *Chem. Abs.*, 1936, **30**, 5773; *J. Inst. Pet. Tech.*, 1936, **22**, 298A.

[67] British P. 411,198, 1932 to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1934, 791.

[68] M. Mueller-Cunradi and M. Otto, U. S. P. 2,065,474, Dec. 22, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, **31**, 1040.

Polymerization of Liquid Olefins. The higher olefins boiling in the gasoline or kerosene range would appear to furnish, on polymerization, fractions whose properties are somewhat superior to those obtained from similarly treated gaseous olefins. Petrov and Pozhiltzeva[69] secured oils from the cracked kerosene fraction of sapropelite tar oils in very low yields at atmospheric conditions, but under seven atmospheres pressure and at a temperature of 200°C. a 25 per cent yield of a fraction boiling above 240°C. was obtained. The complicated nature of the original cracked distillate leads to complex polymerization and condensations; detailed examination of the fractions led to the conclusion that the olefins are polymerized to naphthenes, and also are converted, with aromatics present, to alkylaromatic hydrocarbons. A condensation of naphthenes with olefins also takes place, forming in all probability, dicyclic naphthenic hydrocarbons. They report that the oils obtained by condensing olefins with naphthalene are very similar, particularly in their temperature-viscosity characteristics, to Davis and Blackwood's Paraflow.[70]



Courtesy Industrial and Engineering Chemistry

FIG. 64.—Plant for Synthesis of Lubricating Oils by Olefin Polymerization with Aluminum Chloride. (F. W. Sullivan, Jr., V. Voorhees, A. W. Neeley and R. V. Shankland)

Zherdeva[71] investigated the possibilities of making aviation lubricants from the kerosene distillates produced in the cracking of paraffin wax and slop oils. Condensation was effected by treatment with 3 per cent of anhydrous aluminum chloride at 60° to 70°C., forming two layers. From the upper layer, basic oils were obtained by concentrating after neutralization and water washing. The lower layer (about 10 per cent of the total) consisted of a complex formed between the catalyst and various hydrocarbons. Decomposed with water, this yielded a dark oil. It was considered that the presence of aromatic hydrocarbons in the original material affected the quality of the product adversely. Good lubricants were obtained from a kerosene fraction secured by cracking paraffin bottoms, however.

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[69] A. D. Petrov and E. A. Pozhiltzeva, *J. Appl. Chem. (U.S.S.R.)*, 1933, 6, 1140; *Chem. Abs.*, 1934, **28**, 1176; *Brit. Chem. Abs.* B, 1934, 229.

[70] G. H. B. Davis and A. J. Blackwood, *Ind. Eng. Chem.*, 1931, **23**, 1452; *Chem. Abs.*, 1932, **26**, 1107; *Brit. Chem. Abs.* B, 1932, 169. For a discussion of Paraflow, see Chapter 30.

[71] L. Zherdeva, *Neft. Khoz.*, 1934, **26**, 53; *Chem. Abs.*, 1934, **28**, 7507; *Foreign Petr. Tech.*, 1933, **1** (1), 3; *J. Inst. Pet. Tech.*, 1934, **20**, 366A.

Technical Processes for Synthesis of Lubricants. For this type of synthesis, Sullivan and Voorhees[72] suggested employment of a distillate having a final boiling point under 260°C. produced by vapor-phase cracking of high-wax content oils (such as slack wax or sweater oil). By polymerizing such fractions with one-half to 4 per cent of anhydrous aluminum chloride at 80°C. for 15 to 20 hours, or between 38° and 80°C. for not more than 50 hours, lubricating oils of low viscosity-temperature coefficients, low specific gravity and low carbon-forming tendency are obtained. Chittick[73] reports that treating a cracked gasoline with a small amount of aluminum chloride (about 0.5 per cent) serves to convert the gum-forming constituents present into lubricant-like bodies. Polymerization is carried out at a temperature of about 260°C. under conditions which permit the hydrocarbons of the gasoline range to distill off. The residual oil formed is washed with water and caustic alkali. After treatment with fuller's earth, it may be used as a lubricating oil blending stock.

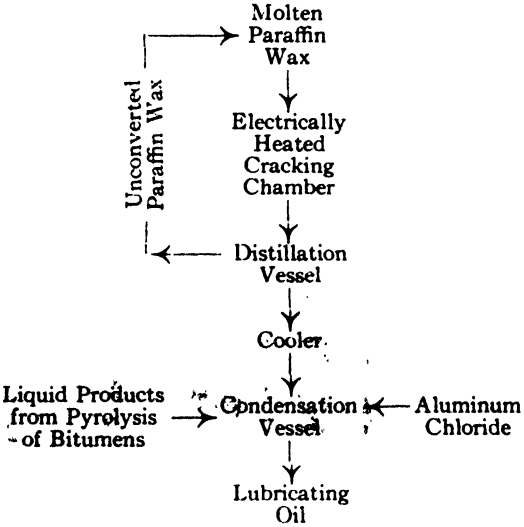

FIG. 65.—Flow Diagram for Condensation of Aromatic Hydrocarbon Material with Higher Olefins from Paraffin Wax. (H. Zorn, M. Müller-Cunradi and W. Rosinsky)

Oils have been produced by condensing the unsaturated liquid products of vapor-phase cracking of paraffin wax with various cyclic hydrocarbons such as naphthalene, anthracene or cyclohexane. Reaction takes place at temperatures up to 150°C. in the presence of one of the Friedel-Crafts agents.[74]

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[72] F. W. Sullivan and V. Voorhees, U. S. P. 1,955,260, April 17, 1934, to Standard Oil Co. of Indiana; *Chem. Abs.*, 1934, 28, 3889; *J. Inst. Pet. Tech.*, 1934, 20, 427A.

[73] M. B. Chittick, U. S. P. 2,048,992, July 28, 1936, to Pure Oil Co.; *Chem. Abs.*, 1936, 30, 6551; *J. Inst. Pet. Tech.*, 1936, 22, 456A.

[74] W. Pungs, H. Rabe and H. Zorn, U. S. P. 1,938,088, Dec. 5, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1182; *J. Inst. Pet. Tech.*, 1934, 20, 114A.

It has been suggested that liquid hydrocarbons from the pyrolysis of bituminous materials be condensed with higher liquid aliphatic olefins (such as may be formed by cracking paraffin wax). Condensation is effected in two stages, part of the product being treated in the first stage. This treated portion is then mixed with the remainder of the material prior to the final condensation.[75] Halloran and Chappell[76] recommend the use of unsaturated hydrocarbons extracted by the treatment of petroleum with sulphur dioxide. Egloff[77] has flash distilled the residues produced in cracking heavy oils, and contacted the vapors with aluminum chloride. Osterstrom's process[78] reacts a mixture of the residual oil derived from cracking paraffin wax and a fraction of unsaturated hydrocarbons (boiling at 215° to 370°C.) from the vapor-phase cracking of gas oil.

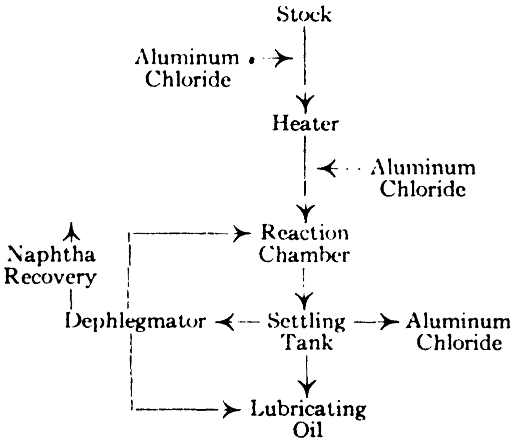

FIG. 66.—Flow Scheme for Lubricating Oil Synthesis from Sulphur Dioxide Extracts. (R. A. Halloran and M. L. Chappell)

The list of suggested raw materials is quite diverse. Such substances as cracking or hydrogenation products of mineral oil and coal, paraffin wax and petroleum jelly, alcohols, organic acids or esters of high molecular weight can all be converted to a species of lubricating oils by polymerization or condensation in the presence of the metal halides; this condensation being preceded in some cases by halogenation.[79] The products obtained may be given greater resistance to oxidation by the addition of 0.05 to 10 per cent of certain organic substances (such as aromatic ethers or cyclic compounds containing sulphur) or elementary sulphur to the raw materials.[80]

The fraction of a liquid-phase product boiling between 150° and 450°C. (after purification by a solvent process) can be cracked a second time in the vapor phase, sometimes with the aid of catalysts, to yield a mixture of unsaturated hydrocarbons which can be polymerized by aluminum chloride to produce lubricants.[81]

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[75] H. Zorn, M. Müller-Cunradi and W. Rosinsky, U. S. P. 1,965,952, July 10, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5658; *J. Inst. Pet. Tech.*, 1934, **20**, 540A.

[76] R. A. Halloran and M. L. Chappell, U. S. P. 1,893,774, Jan. 10, 1933, to Standard Oil Co. of California; *Brit. Chem. Abs.* **B**, 1933, 903; *Chem. Abs.*, 1933, **27**, 2295.

[77] G. Egloff, U. S. P. 1,960,625, May 29, 1934, to Universal Oil Products Co.; *Chem. Abs.*, 1934, **28**, 4591; *Brit. Chem. Abs.* **B**, 1935, 295.

[78] R. C. Osterstrom, U. S. P. 1,973,824, Sept. 18, 1934, to Pure Oil Co.; *Brit. Chem. Abs.* **B**, 1935, 760; *Chem. Abs.*, 1934, **28**, 6998.

[79] British P. 435,548, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1935, 1127.

[80] British P. 435,597 and 435,598, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1935, 1127.

Fischer, Koch and Wiedeking[82] have prepared lubricants from dichlorinated paraffinic oils (such as the so-called "Kogasin" synthesized[83] by catalytic combination of carbon monoxide and hydrogen) utilizing activated aluminum chloride. The oils so prepared are said to compare favorably with natural products as regards resistance to oxidation, coking residue and pour-point.

It is frequently advantageous to purify the materials to be polymerized before they have undergone this treatment. Many crude olefin mixtures will, under catalysis, release corrosive substances damaging to the equipment; in others there are impurities which are more readily removed before the molecular weights have been increased.

One type of purification process recommends treatment of the cracked distillates with 60° Bé. sulphuric acid, followed by 20° Bé. alkali prior to polymerization.[84] However, purification may be attained by a preliminary treatment with not more than 2 per cent of the catalyst to be used, at a temperature not lower than that planned for the polymerization proper. Thus, the 65° to 75°C. fraction of a vapor-phase cracked gasoline may be treated at 70°C. with one gram of aluminum chloride per 100 cc. of liquid, the mixture distilled and the distillate then polymerized with 4 grams of the chloride per 100 cc. at 30°C. for 22 hours.[85]

A modification, involving the use of an ethylene-aluminum chloride complex as catalyst instead of the halide itself, has been suggested by Haeuber for the conversion of cracked distillates at temperatures of 100 to 180°C.[86] Martin, Grimme and Koppelmann,[87] on the other hand, suggest preparing a catalyst for cracking processes by the interaction of aluminum metal and hydrogen chloride. The metal is suspended in a substance capable of undergoing the Friedel-Crafts reaction, such as benzene, in the presence of a small amount of aluminum chloride. Hydrogen chloride gas is bubbled in, forming a complex said to be suitable for use as a cracking catalyst. Since the halide catalysts are destroyed by water, it is important that they be protected from moist gases. Kuentzel and Geissman[88] suggest that this be accomplished by passing the raw olefins over used catalyst before contacting the material with the active polymerizing agent. Caudri[89] reported making a lubricating oil from a cracked gasoline, using a two-stage polymerization process. The distillate, which may contain substances tending to poison the Friedel-Crafts agent, is first contacted with a small amount of the catalyst (e.g., aluminum chloride) at 60° to 130°C. for a time sufficient to polymerize the poisoning substances. The remainder of the material is separated off, and treated with a further quantity of aluminum chloride to bring about polymerization to produce a lubricating oil.

By heating the unsaturated hydrocarbons with a metal halide at a temperature lower than 200°C. with an oil-miscible promoter (such as carbon tetrachloride, methyl chloride or amyl chloride) which is capable of yielding hydrogen chloride in the presence of the metal halide, the yield of viscous products may be increased, according to Snow.[90]

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[81] British P. 431,609, 1935, to Bataafsche Petroleum Maatschappij, *J. Inst. Pet. Tech.*, 1935, **21**, 344A; *Brit. Chem. Abs.* B, 1935, 794.

[82] F. Fischer, H. Koch and K. Wiedeking, *Brennstoff-Chem.*, 1934, **15**, 223; *J. Inst. Pet. Tech.*, 1934, **20**, 615A; *Chem. Abs.*, 1934, **28**, 6291.

[83] See Chapter 52.

[84] British P. 399,646, 1933, to Bataafsche Petroleum Maatschappij; *J. Inst. Pet. Tech.*, 1934, **20**, 41A; *Chem. Abs.*, 1934, **28**, 1852.

[85] British P. 414,237, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1935, **29**, 596; *Brit. Chem. Abs.* B, 1934, 1000.

[86] H. Haeuber, U. S. P. 1,971,301, Aug. 21, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 6561; *J. Inst. Pet. Tech.*, 1934, **20**, 582A.

[87] F. Martin, W. Grimme and A. Koppelmann, U. S. P. 2,057,306, Oct. 13, 1936; *Chem. Abs.*, 1936, **30**, 8596.

[88] W. E. Kuentzel and T. A. Geissman, U. S. P. 2,040,658, May 12, 1936, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1936, **30**, 6768; *J. Inst. Pet. Tech.*, 1936, **22**, 307A.

[89] J. M. Caudri, U. S. P. 2,055,425, Sept. 22, 1936, to Shell Development Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 545A; *Chem. Abs.*, 1936, **30**, 7841.

Ayres and Smith[91] have made lubricants, as well as other products (e.g., kerosene and various refined hydrocarbons), by treating petroleum stocks with aluminum chloride (at temperatures not exceeding 150°C.) in the presence of an excess of chlorine or hydrogen chloride.

OTHER POLYMERIZATION PRODUCTS OF OLEFINS

Olefin polymerization can be carried further to give very viscous oils, tarry products and synthetic resins.[92] Some of these may be added to lubricating oils for various reasons, and others, particularly the resins, find use in coating compositions.

The complex hydrocarbon mixture obtained by heating pyrene with aluminum chloride,[93] is said to be capable of imparting a greenish-yellow fluorescence, or bloom, to lubricating oils when added to the extent of about one-thousandth of one per cent. Smith[94] suggests a similar use for materials obtained from chloride sludge formed in the refining of hydrocarbon oils of naphthenic character. Smith's method employs centrifuging, filtering or washing with dilute sulphuric acid and subsequent neutralization to recover the bloom agent in a concentrated form. Rosson and Fasce[95] find that a solid coloring matter, or dye suitable for coloring lubricating oils may be produced by an aluminum chloride condensation. The anhydrous catalyst is allowed to react with a mixture containing an aromatic such as benzene or toluene and also a polycyclic aromatic such as naphthalene or anthracene, at a temperature of 45° to 55°C. The catalyst is separated from the reaction mixture, and the coloring material recovered from the products.

Condensed materials of high molecular weight capable of lowering the pour-point of lubricants may be prepared by the action of the halide catalysts on higher petroleum hydrocarbons. If waxy hydrocarbons, with or without aromatics, are condensed with aluminum chloride and the lighter inactive materials boiling below about 370°C. are separated out, an active pour-point depressant with a mean molecular weight above 1200 may be recovered by a wax-precipitating agent.[96] Similar reactions on paraffin wax,[97] petrolatum[98] and hard or soft paraffin[99] produce stocks valuable in improving the properties of lubricants.

Pevere[100] states that a tarry residue derived from the aluminum chloride treatment of an aromatic hydrocarbon may have application in dewaxing lubricating oil. The condensation product resulting from this treatment is distilled under high vacuum to obtain a residue consisting essentially of a tarry material which is not volatile at 310°C. under 10 mm. of mercury pressure. It is reported that this material may be added in proportion of less than 5 per cent to the oil to be treated, to bring about precipitation of the wax on cooling.

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[90] H. R. Snow, U. S. P. 1,970,402, Aug. 14, 1934, to Standard Oil Co. of Indiana; *Chem. Abs.*, 1934, **28**, 6297; *J. Inst. Pet. Tech.*, 1934, **20**, 583A.

[91] E. Ayres and H. G. Smith, British P. 398,032, 1932, to Gulf Refining Co.; *Brit .Chem. Abs.* B, 1933, 1045; *Chem. Abs.*, 1934, **28**, 1519.

[92] See also Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[93] S. F. Birch, British P. 438,425, 1934, to Anglo-Iranian Oil Co.; *Brit. Chem. Abs.* B, 1936, 137; *Chem. Abs.*, 1936, **30**, 2748.

[94] H. G. Smith, U. S. P. 1,944,851, Jan. 23, 1934, to Gulf Refining Co.; *Brit. Chem. Abs.* B, 1934, 1002; *Chem. Abs.*, 1934, **28**, 2176.

[95] M. M. Rosson and E. V. Fasce, U. S. P. 2,055,634, Sept. 29, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 7870.

[96] R. G. Sloane, British P. 402,253, 1932, to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1934, 184; *Chem. Abs.*, 1934, **28**, 3229. For other means of preparing pour-point depressants see Chapters 30 and 34. Also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934, 741.

[97] British P. 415,065, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1934, 952; *Chem. Abs.*, 1935, **29**, 921.

[98] G. H. B. Davis, U. S. P. 1,934,043, Dec. 7, 1933, to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1934, 749; *Chem. Abs.*, 1934, **28**, 632.

[99] German P. 582,853, 1933, to Standard Oil Development Co.; *Chem. Abs.*, 1934, **28**, 891.

[100] E. F. Pevere, Canadian P. 357,661, 1936, to Texaco Development Corp.; *Chem. Abs.*, 1936, **30**, 4662. British P. 437,779, 1935; *Brit. Chem. Abs.* B, 1936, 54; *Chem. Abs.*, 1936, **30**, 3630. See also R. C. Osterstrom and C. R. Wagner, U. S. P. 1,967,099, July 17, 1934, to Pure Oil Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 540A; *Chem. Abs.*, 1934, **28**, 5976.

Double compounds of aluminum chloride and an olefin have been proposed as agents for the removal of gum-forming compounds from gasoline.[101] Sumpter has removed these compounds with the aid of aluminum chloride and an alkali metal or alkali-earth metal chloride, such as potassium, sodium or barium chloride, in equivalent molecular proportions.

Varshavskii and Shenfinkel[102] state that a drying oil may be obtained by treating with cold water the aluminum chloride complex resulting from the polymerization of a gasoline distillate (polymerized at 100° to 120°C. for four hours). Waterman[103] has prepared an analogous drying oil from a cracked mineral oil containing polyolefins. The oil is treated with a metal halide (e.g., $AlCl_3$) at below 65°C., and the polymerized products are separated from the sludge formed in the reaction. This material is neutralized, and subjected to a non-cracking distillation, to secure a residue in which the drying components are concentrated.

Waterman, Leenderste and Ligtenberg[104] treated a cracked distillate with aluminum chloride at room temperature for four to five hours. Under these conditions polymerization proceeds to a resin soluble in organic solvents and capable of emulsification in ammoniacal water to a stable, spongy composition.

Thomas[105] has worked with a type of resin produced by the co-polymerization of an olefin and a diolefin. Using hexadiene and olefins such as trimethylethylene or ethylene, the substances are reacted in the presence of aluminum chloride. The finely divided catalyst is fed in slowly, and cooling is provided to maintain the temperature between 25° and 35°C., as below 20°C. the reaction is slow and the product soft. Temperatures above 20°C. produce harder resins, but above 65°C. the color is poorer. The amount of catalyst required varies with the size of the batch; with 25 gallon operations, 1.4 per cent of catalyst is used, while with 100 cc. runs, 3.5 per cent of catalyst is needed. Treatment lasting 4 to 6 hours gives optimum results. The product from this treatment is neutralized in alcoholic ammonia, yielding a granular precipitate. The addition of a hydrocarbon solvent (such as benzene) and filtration free the resinous material of decomposition products from the metal chloride. The resin can be recovered from the hydrocarbon solvent.[106] This same investigator has reported[107] that resins of this type are reactive, showing high iodine numbers. In consequence, they can be further reacted with glycerol and castor oil to produce a resin soluble in varnish solvents which dries to produce a film said to be clear and elastic and resistant to acids and alkalies.

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[101] British P. 410,874, 1934, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech.*, 1934, **20**, 458A; *Brit. Chem. Abs.* B, 1934, 790.

[102] S. L. Varshavskii and I. K. Shenfinkel, Russian P. 39,899, 1934; *J. Inst. Pet. Tech.*, 1936, **22**, 322A; *Chem. Abs.*, 1936, **30**, 3668.

[103] H. I. Waterman, Canadian P. 360,536, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 7835.

[104] H. I. Waterman, J. J. Leendertse and H. I. Ligtenberg, *Chem. Weekblad.*, 1935, **32**, 342; *Chem. Abs.*, 1936, **30**, 186; *Brit. Chem. Abs.* B, 1935, 735.

[105] C. A. Thomas, U. S. P. 2,039,363, May 5, 1936, to Monsanto Petroleum Chemicals, Inc.; *Chem. Abs.*, 1936, **30**, 4237.

[106] C. A. Thomas and W. H. Carmody U. S. P. 2,060,404, Nov. 10, 1936, to Monsanto Petroleum Chemicals, Inc.; *Chem. Abs.*, 1937, **31**, 480) state that synthetic resins of the type prepared by polymerization of diolefins in the presence of a Friedel-Crafts agent may be decolorized by a solvent process. The resin is pulverized and taken up in a non-aromatic hydrocarbon solvent such as pentane, hexane or naphtha, and agitated for about 15 minutes with an active bleaching clay. The solution is then separated from the clay and coloring matter, and the solvent removed (e.g., by distillation). The decolorization is said to be more satisfactory when low boiling solvents such as pentane or hexane are employed, than when the higher fractions such as octane or naphtha are used. The final decolorized product has varnish making properties substantially similar to those of the original untreated resin, the investigators state.

[107] C. A. Thomas, U. S. P. 2,039,367, May 5, 1936, to Monsanto Petroleum Chemicals, Inc.; *Chem. Abs.*, 1936, **30**, 4237. For previous work of this type see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935, 190 *et seq.*, 225.

Berger[108] has suggested that a resin may be produced from the halide sludge obtained in aluminum chloride refining processes applied to hydrocarbon oils. The sludge produced by treating a cylinder oil stock with the catalyst for 2 hours at 120°C. was used as raw material in one instance. This was freed of entrained oil by extraction with solvent naphtha, and then treated with free chlorine at 95°C. for four hours. At the end of this time the mass was washed in hydrochloric acid, and subsequently decomposed into a water solution and a solid, dark-brown, thermoplastic substance insoluble in any ordinary solvent. It is reported that carbon tetrachloride, chlorinated naphtha, chlorinated propane or pentachlorobutane may be used in place of free chlorine in this process.[109]

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[108] H. G. Berger, U. S. P. 2,043,824, June 9, 1936, to Socony Vacuum Oil Co.; *Chem. Abs.*, 1936, 30, 5327.

[109] See Chapter 28. Also, Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., 1935, 164, *et. seq.*

Chapter 7

Production of Hydrogen and Carbon by Pyrolysis of Hydrocarbons

The thermal decomposition of all hydrocarbons produces, ultimately, carbon and hydrogen. In the temperature range 600-1400°C., however, methane is also secured, and the proportions of the two gaseous constituents (methane and hydrogen) at sufficiently long contact times are defined by the equation,

$$CH_4 \rightleftharpoons C + 2H_2$$

Equilibrium in this system corresponds with almost complete decomposition of methane at slightly above 1000°C., but in actual practice higher temperatures are necessary. In considering the yields of carbon and hydrogen from hydrocarbons, this reaction is, therefore, of prime importance.

In addition to the temperature factor, the pyrolysis of methane is influenced by the time of contact, pressure, the presence of catalytically active substances and the use of diluents or hydrogen. In particular, the time factor exerts a very great influence both on the character of the products and the extent of dissociation. In the temperature range of 1000-1200°C., methane decomposes mainly into acetylene, ethylene and aromatic oils at contact times of the order of 0.1 second. On the other hand, at heating periods of 40 to 45 seconds at 1100°C. (or 5 seconds at 1250°C.) complete decomposition of methane into its elements can be achieved. The carbon obtained is gray, has a high apparent density and is unsuitable as a pigment or as a substitute for lampblack. According to Padovani,[1] this material is crystalline and graphitic. Metallic surfaces favor graphitization and the carbon tends to form a thick crust on the walls of the reaction tube. It has been shown by the same investigator that a more useful form may be produced, together with aromatic oils, by conducting the pyrolysis of methane at contact times intermediate between those necessary for the complete decomposition on the one hand and, on the other, for the optimum production of aromatic liquids. By cracking methane under these conditions at 1100°C., in such a way that most of the carbon formed was carried off in the gas, he obtained from one cubic meter about 200 g. of carbon black, 35 g. of aromatic oils and 1.4 cubic meters of gas consisting of two-thirds hydrogen and one-third residual methane.

Catalysts which accelerate the decomposition of methane include metals such as iron or nickel, and graphitic carbon.[2] Certain special contact agents have been advocated, but their value is rather doubtful, since frequent elimination of deposited carbon (from them), by oxidation with air or by steam, is usually necessary. A catalyst consisting of 5 parts ferric oxide, 2 parts calcium carbonate, 1 part nickel oxide and 0.5 part manganese dioxide supported on iron filings has been used by Candea and Kühn[3] for cracking methane at 800-1000°C. In this instance, the carbon was removed by steam. However, the dissociation of methane appeared to take place chiefly at the exposed surface of the reaction chamber and there was reason to believe that catalytic action was of secondary importance compared with the effect of increasing the heating area. Hence, industrial operation is usually carried out in the presence of refractory materials of large surface and high heat content.

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[1] C. Padovani, *Proc. 3rd Intern. Conf. Bituminous Coal*, 1932, 1, 910; *Chem. Abs.*, 1932, 26, 4935; *Brit. Chem. Abs.* B, 1932, 1064. *Chimie et industrie*, 1931, March Spec. No., 317; *Chem. Abs.*, 1931, 25, 3411.

[2] N. I. Kobozev, L. I. Kashtanov and S. M. Kobrin. *J. Gen. Chem. (U.S.S.R.)*, 1935, 5, 143; *Chem. Abs.*, 1935, 29, 4920; *Brit. Chem. Abs.* B, 1935, 714.

With regard to the other factors influencing the separation of methane into its elements, dilution with an inert gas such as nitrogen slows down reaction by reducing the partial pressure of the hydrocarbon. It also decreases the velocity of the reverse reaction (combination of carbon and hydrogen) by exerting the same effect on hydrogen, these two opposing influences tending to compensate each other to some extent. Dilution with hydrogen reduces the speed of dissociation and increases the rate of combination so that, in effect, it retards the transformation of methane into its elements in two ways; moreover, this effect becomes more and more pronounced as complete reaction, $CH_4 \rightarrow C + 2H_2$, is approached.

The successful production of carbon black by thermal decomposition appears to depend on the use of a brief contact time, combined with some method of preventing deposition of the carbon on the highly heated walls of the chamber. Any attempt to produce carbon in a heated tube invariably results in the settling of a layer of hard, gray, lustrous material on the walls, which, owing to its poor heat conductivity, soon insulates the reaction zone from the source of heat. In the Thermatomic[4] process decomposition of hydrocarbons takes place in a refractory checkerwork and the carbon black is swept out of the cracking furnace in the gas stream. Any carbon deposited on the checkerwork is burnt out in the subsequent cycle, in which the refractory material is heated to about 1300°C. by gas firing. In some instances a blanket of hot gas, separating the hydrocarbon from highly heated walls, and thereby simulating a wall-free reaction space, is employed to prevent the formation of hard carbon on the sides of the reaction tube. In the "Gastex" process,[5] parallel streams of hydrocarbon gas and air are passed through the reactor in such a way that combustion occurs at the air-gas interface which supplies the heat to decompose the hydrocarbon. The latter does not come in contact with the walls of the system, the energy for decomposition being supplied by flames.

A somewhat similar method has been used by Pidgeon[6] for producing carbon black from the lower paraffin hydrocarbons in what is virtually a wall-free reaction space. He carried out decomposition in porous tubes, through which a certain amount of inert gas was diffused. This was accomplished by placing the refractory tube in a gas-fired furnace, in which the pressure (of the inert gas) was greater than that in the tube, thus maintaining a blanket of flue gas to separate decomposing hydrocarbon from the walls of the reaction tube.[7] Under these conditions, about 19 lbs. of carbon black were obtained from 1000 cubic feet of methane at a temperature of 1350-1400°C. and an apparent contact time of 0.25 second. By dissociation of a mixture of 70 per cent propane and 30 per cent butane at about 1350°C. and an apparent contact time of 0.1 to 0.2 second, yields of carbon black amounting to 60 lbs. per 1000 cu. ft. (60 per cent of theoretical) were secured.

[3] C. Candea and J. Kühn, *Chimie et industrie*, 1933, Special No., 861; *Chem. Abs.*, 1934, **28**, 287; *Brit. Chem. Abs.* B, 1933, 953.

[4] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[5] I. Drogin, *India Rubber J.*, 1935, **90**, 259; *Chem. Abs.*, 1935, **29**, 8249; *Brit. Chem. Abs.* B, 1935, 932.

[6] L. M. Pidgeon, *Can. J. Research*, 1935, **13B**, 351; *Chem. Abs.*, 1936, **30**, 1953.

[7] See P. K. Frolich, U. S. P. 2,062,358, Dec. 1, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1937, **31**, 823. Canadian P. 348,890.

The particle size of the carbon depended largely on the time of contact, more prolonged heating resulting in larger particles. The carbon blacks made by this method were similar to soft blacks in that they had a high density, low sorptive power, accelerated the cure of rubber stock and gave similar resistance to aging and abrasion. However, in their ability to impart stiffness to rubber stock, they occupied a position intermediate between the channel and soft blacks.

For the commercial production of both carbon and hydrogen by thermal decomposition, natural gas, especially the so-called "dry" gases, constitutes an appropriate raw material because of its abundance and low price. An ideal process of this type would be one capable of yielding simultaneously relatively pure hydrogen gas and high-grade carbon, the latter useful as a substitute for carbon black or lampblack. Unfortunately, the available data seem to indicate that under conditions which give a gas rich in hydrogen, the carbon obtained is of poor quality and valueless, except as a fuel. On the other hand, procedures which favor the formation of more valuable types of carbon, do not yield at the same time a very pure hydrogen. In the Thermatomic process,[8] 1000 cubic feet of natural gas furnishes 1800 cubic feet of a gas containing 81 per cent of hydrogen, 6 per cent methane, and a residue of nitrogen, oxygen and oxides of carbon. Also, it has been reported that small quantities of acenaphthylene and pyrene are secured from this process.[9] For the preparation of hydrogen from natural gas, the catalytic reactions with steam,[10]

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

and

$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2$$

or incomplete combustion,

$$CH_4 + \tfrac{1}{2}O_2 \longrightarrow CO + 2H_2$$

would appear to be more applicable.

In the technical production of hydrogen from hydrocarbons by pyrolysis, the carbon simultaneously formed is utilized as a fuel. For example, the endothermic decomposition may be carried out in the presence of highly-heated refractory material, on which the carbon is deposited. As soon as the temperature of the contact mass has fallen to a lower limit, the carbon is burnt off by means of an air blow, raising the temperature of the refractory mass in readiness for another dissociation cycle. In processes for the manufacture of higher grade forms of carbon, the hydrogen-containing gas simultaneously formed is usually employed as a fuel.

PRODUCTION OF CARBON AND HYDROGEN BY SIMPLE THERMAL DECOMPOSITION

Spear and Moore[11] obtained carbon black by separately preheating natural gas and a diluent gas, e.g., hydrogen, mixing the two, and effecting decomposition in a heated zone of refractory checkerwork. The products were rapidly cooled by water sprays and passed to a separator. Dilution of a hydrocarbon gas with at least twice its volume of hydrogen, followed by passage of the mixture over highly heated surfaces (see Fig. 67) is recommended by the same investigators.[12] The black secured is reported as a new product,[13] having an apparent density of about

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[8] See Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York. 1934.

[9] A. W. Campbell, N. H. Cromwell and J. J. Hager, *J.A.C.S.*, 1936, **58**, 1051; *J. Inst. Pet. Tech.*, 1936, **22**, 396A; *Chem. Abs.*, 1936, **30**, 5215; *Brit. Chem. Abs.* **B**, 1936, 774.

[10] See Chapter 10 for a discussion of these reactions.

[11] E. B. Spear and R. L. Moore, U. S. P. 1,911,033, May 23, 1933, to Thermatomic Carbon Co.; *Brit. Chem. Abs.* **B**, 1934, 229; *Chem. Abs.*, 1933, **27**, 4041.

[12] E. B. Spear and R. L. Moore, U. S. P. 1,987,643, Jan. 15, 1935, to Thermatomic Carbon Co.; *Chem. Abs.*, 1935, **29**, 1595; *Brit. Chem. Abs.* **B**, 1936, 52.

[13] E. B. Spear and R. L. Moore, U. S. P. 1,987,644, Jan. 15, 1935, to Thermatomic Carbon Co.; *Brit. Chem. Abs.* **B**, 1936, 52; *Chem. Abs.*, 1935, **29**, 1595.

0.37 and a maximum loading value[14] in rubber (when compounded as a reinforcing agent) in excess of 100 but not substantially higher than 150. The use of a checker-filled converter is also reported by Frenkel.[15] In this case the product is collected, mixed with water and subjected to high pressure. It is then sprayed with a stream of hot combustion gases to effect flash evaporation of the water. Brownlee[16] suggests that after decomposition of natural gas by contact with hot checkerwork for a short period, the gaseous yield be quickly cooled by refrigerated residual gas from a previous operation. The resulting black has a greater tinting power,[17] lower apparent density and a flocculence not greater than that of channel black. Reed[18] makes use of a vertical chamber packed with checkerwork constructed of units having wedge-shaped edges which project in a direction counter to that of the gas flow (see Fig. 68). The checkerwork thus presents only inclined or vertical surfaces to the flow, has no pockets in which the carbon can collect and no horizontal surfaces capable of causing abrupt contact and separation of carbon. The system is heated periodically by direct combustion. Wilcox[19] effects the conversion

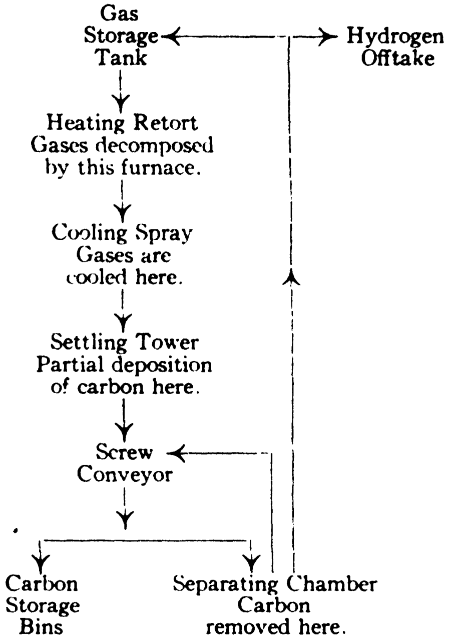

FIG. 67.—Flow Diagram for Carbon and Hydrogen Production by Thermal Decomposition of Hydrocarbons. (E. B. Spear and R. L. Moore)

of natural gas or other hydrocarbon gases into carbon black and aromatic compounds by passage through an elongated conduit with a contact time of 1 to 3 seconds. The refractory tube is internally heated to 980-1200°C. by combustion gases. The hydrocarbon is decomposed while flowing in a direction countercurrent to the heating gases and the carbon black is recovered from the partially cooled gaseous product by electrostatic precipitation, and subjected to further cooling and oil-scrubbing to remove liquid hydrocarbons. In an effort to secure the maximum amount of carbon black, Willien[20] conducted natural gas without steam through a

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[14] Loading value is used to designate the volume of carbon black that can be incorporated in 100 volumes of rubber.

[15] G. A. Frenkel, Canadian P. 337,707, 1933, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 1822. U. S. P. 1,990,228, Feb. 5, 1935; *Brit. Chem. Abs.* B, 1936, 85; *Chem. Abs.*, 1935, **29**, 1948.

[16] R. H. Brownlee, U. S. P. 1,925,130, Sept. 5, 1933; *Brit. Chem. Abs.* B, 1934, 532; *Chem. Abs.*, 1933, **27**, 5491.

[17] R. H. Brownlee, U. S. P. 1,920,352, Aug. 1, 1933; *Brit. Chem. Abs.* B, 1934, 488; *Chem. Abs.*, 1933, **27**, 4889.

[18] F. C. Reed, U. S. P. 1,980,827, Nov. 13, 1934; *Brit. Chem. Abs.* B, 1935, 982; *Chem. Abs.*, 1935, **29**, 564.

[19] W. D. Wilcox, U. S. P. 1,916,291, July 4, 1933; *Brit. Chem. Abs.* B, 1934, 488; *Chem. Abs.*, 1933, **27**, 4639.

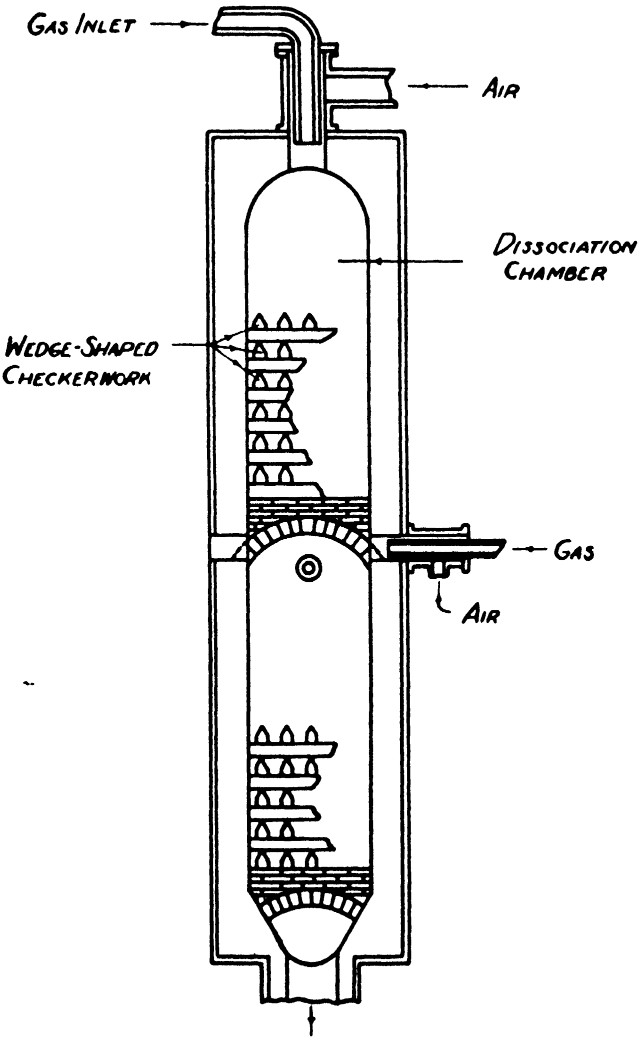

FIG. 68.—Sketch of Dissociation Chamber Containing Wedge-shaped Checkerwork for Carbon Black Formation. (F. C. Reed)

bed of incandescent coke. The reformed gas passed through a Cottrell precipitator and a Cyclone dust collector which recovered 98 per cent of the carbon black. Richardson,[21] to control the relative amounts of carbon black and gaseous products, suggests that a mixture of steam and hydrocarbon gas in the proportion 3:1 by volume be heated sufficiently to effect thermal decomposition.

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[20] L. J. Willien, *Am. Gas. Assoc. Proc.*, 1935, 17, 779; *Chem. Abs.*, 1936, 30, 3967; *Brit. Chem. Abs.* B, 1936, 726.

A process for the manufacture of a gas rich in hydrogen (and free from carbon black) from natural gas or oil-still gas is described by Terzian,[21a] who brings about the decomposition in the presence of a heated bed of fuel (coke), which is intermittently air-blasted. All liberated carbon is retained for subsequent utilization during the air-blow, and the porosity of the fuel bed is preserved by reducing the temperature of its surface prior to the passage of the hydrocarbon gas. Towne[22] suggests activated alumina or bauxite, pumice or fuller's earth instead of coke for this type of treatment.

To obtain large percentages of hydrogen by pyrolysis of hydrocarbons it is advocated that the gaseous raw material be conducted through a cylindrical mass of hot crushed refractory material arranged so that the central portion of the mass is more porous than succeeding outward portions, the object being to allow longer periods of contact in the cooler areas so that there may be more uniform cracking efficiency throughout the refractory material.[22a]

As a raw material from which hydrogen may be obtained, Turner and Keene[23] propose Pennsylvania anthracite. When samples were heated slowly to 1036°C. under an initial pressure of less than 1 mm. the volatile matter contained 75-79 per cent hydrogen, applicable for welding purposes and hydrogenation.

Pyrolysis of acetylene, with or without air,[24] and at moderate temperatures (180°C.), has been used to make a special quality of carbon black, usually referred to as acetylene black. Day[25] has found that the black secured from purified acetylene had an ash content of 0.01 to 0.05 per cent, and could be used for oxidation rate studies.

DECOMPOSITION EFFECTED BY PARTIAL COMBUSTION OF HYDROCARBONS

Part of the heat required for decomposition of hydrocarbons may be obtained by partial combustion of the hydrocarbons either with air or oxygen-containing gases. The usual methods of manufacturing carbon black are based on this principle, the carbon being formed by thermal decomposition of unburned hydrocarbons and rapidly removed from the flame zone by impingement on cooled surfaces. Incomplete combustion may also be employed for producing mixtures of hydrogen and oxides of carbon with or without nitrogen.

The preparation of carbon black by incomplete burning of hydrocarbon gases in small-bore refractory tubes is described by Brownlee (see Fig. 69).[26] Another procedure comprises passing hydrocarbon vapors through a sheet of flame, the latter placed near a radiating surface.[27] Beaver[28] effected partial burning of hydrocarbon gases in a series of narrow, flattened burners mounted in the lower part of a heat-insulated chamber. The burners, which are surrounded by air ducts, are mounted in a row with their longer sides parallel so that the flames radiate mainly to each other. The air supply is regulated to about 40-75 per cent of that required for complete combustion and the chamber is so dimensioned as to give a time of contact in the hot zone of about 0.5 to 1 second. The carbon black is recovered from the gases leaving the stack of the furnace. Partial combustion for the manufacture of carbon black is carried out by Keller[29] in a series of narrow ducts, mounted in parallel, vertical planes in an unobstructed, heat-insulated furnace. The hydrocarbon gas is discharged upward and a regulated supply of air is introduced near the lower end of the gas ducts. Bevelling prevents deposition of carbon on the ends of the gas ducts and facilitates streamline flow of both hydrocarbon gas and air at these points.

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[21] R. S. Richardson, U. S. P. 2,013,699, Sept. 10, 1935, to Chemical Construction Corp.; *Chem. Abs.*, 1935, **29**, 7029.

[21a] H. G. Terzian, U. S. P. 1,956,259, April 24, 1934, to United Gas Improvement Co.; *Chem. Abs.*, 1934, **28**, 4211. See also H. B. Young, *Am. Gas Assoc. Proc.*, 1935, 17, 772; *Chem. Abs.*, 1936, **30**, 3968; *Brit. Chem. Abs.* B, 1936, 726.

[22] C. C. Towne, U. S. P. 2,047,499, July 14, 1936, to The Texas Co.; *Chem. Abs.*, 1936, **30**, 6172.

[22a] G. D. Bagley and H. W. B. de W. Erasmus, U. S. P. 2,071,721, Feb. 23, 1937, to Union Carbide and Carbon Corp. Canadian P. 361,530, 1936, to Electric Metallurgical Co. of Canada, Ltd.; *Chem. Abs.*, 1937, **31**, 1563.

[23] H. G. Turner and W. L. Keene, *Ind. Eng. Chem.*, 1935, **27**, 1373; *Brit. Chem. Abs.* B, 1936, 176; *Chem. Abs.*, 1936, **30**, 267.

[24] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[25] J. E. Day *et al.*, *Ind. Eng. Chem.*, 1936, **28**, 234; *Chem. Abs.*, 1936, **30**, 1954.

[26] R. H. Brownlee, U. S. P. 1,925,131, Sept. 5, 1933; *Brit. Chem. Abs.* B, 1934, 532; *Chem. Abs.*, 1933, **27**, 5491.

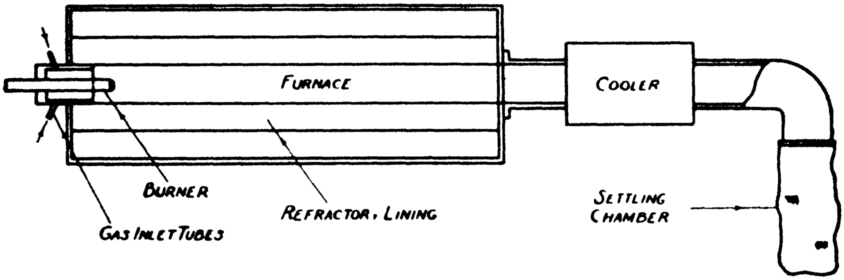

FIG. 69.—Method of Carbon Black Production by Incomplete Burning of Gases in Small-bore Refractory Tubes. (R. H. Brownlee)

The incomplete burning of methane and similar hydrocarbons may be used for the production of mixtures of hydrogen and nitrogen if the carbon monoxide simultaneously formed is removed afterwards from the gas mixture. This latter step may be accomplished, for example, by the conversion of the monoxide to dioxide by reaction with steam (see Fig. 70) followed by elimination of carbon dioxide.[30] The oxidation of methane, expressed by the equation

$$CH_4 + \frac{1}{2}O_2 \longrightarrow CO + 2H_2 + 8 \text{ kg. cal.}$$

is favored by the same catalysts and conditions as the reaction of methane with steam or carbon dioxide. Padovani and Franchetti[31] have investigated this partial oxidation of pure methane and gases of low methane content. In the presence of a nickel catalyst and at space velocities of the order of 500 (i.e., ratio of gas velocity to space), results closely corresponding with the equilibrium values were obtained at 850-950°C. Operation with methane at 900°C. yielded gaseous products containing less than 1 per cent of the hydrocarbon. For the manufacture of carbon black and a mixture of hydrogen and nitrogen in controlled proportions, Wilcox[32] subjects hydrocarbon gases to partial decomposition by passage through conduits heated to progressively higher temperatures. After removing entrained carbon, the gases are diluted with steam and incompletely burned with measured amounts of preheated air. Contact agents such as nickel or iron may be used. The efficiency of a promoter of nickel for the partial combustion of natural gas to carbon monoxide and hydrogen has been investigated.[33] The reaction chamber consisted of a steel cylinder with a lining of refractory fire-clay brick. The lower portion was packed with fire-clay brick and the upper part with nickel catalyst and pieces of fire clay. In the procedure, a mixture of natural gas and steam was conducted into the lower part of the furnace and passed upward. The gases were heated by the hot packing and the contact agent, and were led from the upper portion of the chamber at 1100°C. When the packing had cooled, the conversion process was interrupted and the chamber reheated by combustion of natural gas with excess air. It was stated that in this manner 1.9 cubic meters of steam were admixed with 1 cubic meter of natural gas to yield 3.3 cubic meters of gas containing 64 per cent of hydrogen and 22 per cent of carbon monoxide. Partial combustion of hydrocarbons in the presence of an electric arc has been proposed by Eisenhut[34] for the manufacture of hydrogen-containing gas. Thus, a cubic meter of methane was admixed with like amounts of air and steam. The mixture was then conducted through an electric arc at 1400°C. (see Fig. 71). As the gases left the arc they were led into a mixing chamber containing baffle plates. In this manner a yield of 4 cubic

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[27] British P. 402,322, 1933, to Bataafsche Petroleum Maatschappij; *J. Inst. Pet. Tech.*, 1934, **20**, 115A; *Chem. Abs.*, 1934, **28**, 3196. French P. 754,767, 1933; *Chem. Abs.*, 1934, **28**, 1483.

[28] D. J. Beaver, U. S. P. 1,902,753, March 21, 1933, to General Atlas Carbon Co.; *Brit. Chem. Abs.* B, 1933, 1044; *Chem. Abs.*, 1933, **27**, 3299.

[29] T. P. Keller, U. S. P. 1,904,469, April 18, 1933, to General Atlas Carbon Co.; *Brit. Chem. Abs.* B, 1933, 1044; *Chem. Abs.*, 1933, **27**, 3567.

[30] Carleton Ellis, *Trans. Am. Inst. Chem. Eng.*, 1930, **25**, 16; *Chem. Abs.*, 1931, **25**, 4636.

[31] C. Padovani and P. Franchetti, *Giorn. chim. ind. applicata*, 1933, **15**, 429; *Brit. Chem. Abs.* A, 1933, 1253; *Chem. Abs.*, 1934, **28**, 2853.

Courtesy American Institute of Chemical Engineers

FIG. 70.—Reactors for Conversion of Carbon Monoxide to Dioxide Prior to Separation from Mixtures with Hydrogen. (Carleton Ellis)

meters of gas consisting of 19.1 per cent of nitrogen, 59.2 per cent of hydrogen and 21.4 per cent of carbon monoxide, together with some unchanged hydrocarbons, was said to be furnished.

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[32] W. D. Wilcox, U. S. P. 1,929,664, Oct. 10, 1933; *Brit. Chem. Abs.* B, 1934, 614; *Chem. Abs.*, 1934, **28**, 269.

[33] V. A. Karzhavin, *Ind. Eng. Chem.*, 1936, **28**, 1042; *Chem. Abs.*, 1936, **30**, 6923. See Fig. 88, Chapter 10.

[34] O. Eisenhut, U. S. P. 2,000.224, May 7, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 3923.

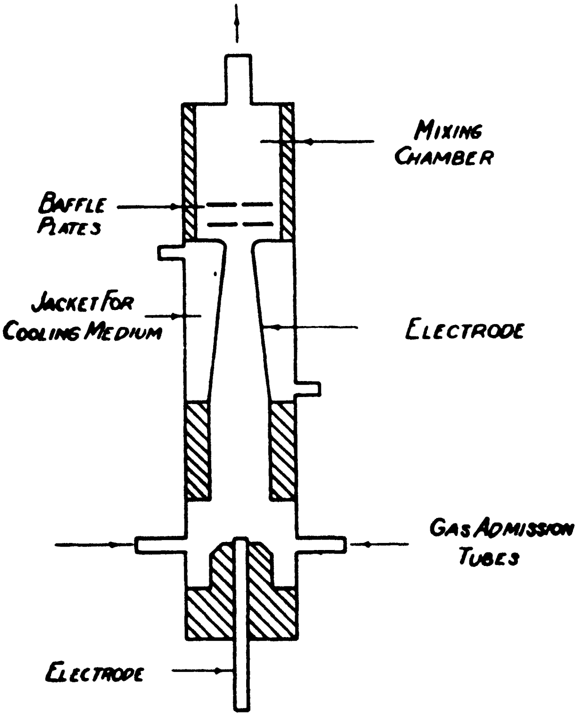

Fig. 71.—Sketch of Apparatus for Partial Combustion of Hydrocarbons in Electric Arc. (O. Eisenhut)

Decomposition by Other Means

A number of methods of preparing carbon blacks by the decomposition of hydrocarbons by electric discharge have been proposed. In the process of Jakosky and Hanson,[35] hydrocarbon oils are conducted through a chamber where they are subjected to the action of a localized high temperature produced by an electric arc. The black is permitted to remain in suspension in the oil and the rate of flow is regulated to maintain its concentration between 8-10 per cent. At higher concentrations, the quality of the black begins to be adversely affected. An apparatus for this procedure, with spaced rotating electrodes (see Fig. 72), has been described by Jakosky and Wieden.[36]

Electrical resistances of high ohmic value are obtained[37] by depositing carbon, furnished by dissociation of a gaseous hydrocarbon (e.g., methane) having a high decomposition temperature (600-800°C.), on an insulating carrier. In this manner formation of an amorphous material is prevented. Excess coating on the carrier is removed by admitting carbon dioxide at a temperature sufficiently low to prevent dissociation of the resulting carbon monoxide.

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[35] J. J. Jakosky and V. F. Hanson, U. S. P. 1,912,373, June 6, 1933, to Electroblacks, Inc.; *Brit. Chem. Abs.* B, 1934, 230. Canadian P. 337,132, 1933; *Chem. Abs.*, 1934, **28**, 1822.

[36] J. J. Jakosky and H. J. Wieden, Jr., U. S. P. 1,931,800, Oct. 24, 1933, to Electroblacks, Inc.; *Chem. Abs.*, 1934, **28**, 589; *Brit. Chem. Abs.* B, 1934, 682.

[37] British P. 399,967, 1933, to Elektrische Glühlampenfabriken Kremenezky A.-G.; *Chem. Abs.*, 1934, **28**, 1794.

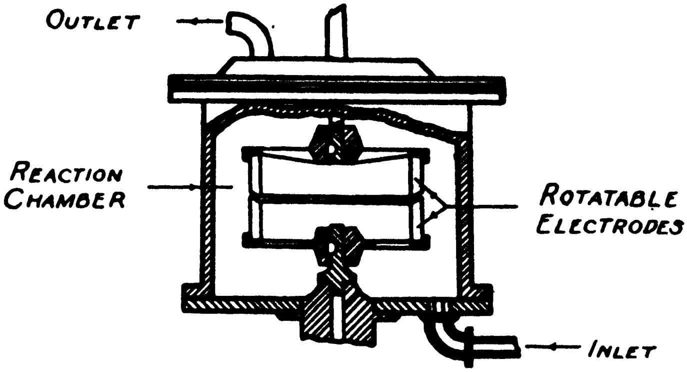

FIG. 72.—Reaction Chamber for Decomposition of Hydrocarbon Oils by Electric Discharge. (J. J. Jakosky and H. J. Wieden, Jr.)

To produce adsorbent carbon, another process is suggested.[38] Coal, lignite, peat or wood may be chlorinated in a suspension of carbon tetrachloride, carbonized by slowly heating to 850°C. and afterwards activated by steam.

DECOMPOSITIONS EFFECTED IN THE PRESENCE OF CATALYSTS

In the pyrolysis of hydrocarbons (such as methane) for the production of hydrogen, it may be expected that the rate of decomposition could be increased by catalysts. In practice, however, the activity of contact agents in reactions of this sort is speedily suppressed by the formation of a protective deposit of carbon, which must be periodically removed by oxidation with air or by passage of steam at high temperatures. Finkel'shtein and Zabolotzkiĭ[39] report the use of fireclay containing 12 per cent nickel oxide, 2 per cent chromium oxide and 3 per cent copper oxide. This catalyst, though not rendered inactive by hydrogen sulphide, will lose its activity if the soot is not eliminated at intervals by steam, forming water gas.

Candea and Kühn[40] found that a good catalyst for the decomposition of methane into its elements at 800-1000°C. was one containing ferric oxide, calcium carbonate, nickel oxide and manganese dioxide in the proportions 10, 4, 2 and 1. Another, consisting of a mixture of 100 parts of aluminum hydroxide, 20 parts of boric acid and 20 parts of silica, is satisfactory for the production of hydrogen from methane at a temperature of about 1200-1250°C.[41] The activity of copper oxide and tin dioxide in the decomposition of natural gas has been studied.[42] When using copper oxide, the rate of flow of the gas was 3 liters per hour. It was said the conversion of the natural gas to carbon and hydrogen began at 400°C. and was complete at 720°C. Employing the same rate of flow of the gas with tin dioxide, it was reported that decomposition took place between 700 and 910°C. but was not complete, even at the latter temperature.

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[38] A. McCulloch and R. E. Hargraves, French P. 765,716, 1934; *Chem. Abs.*, 1934, **28**, 6956. British P. 412,209, 1934; *Chem. Abs.*, 1935, **29**, 564; *Brit. Chem. Abs.* **B**, 1934, 821.

[39] V. S. Finkel'shtein and T. V. Zabolotzkiĭ, *Ukrain. Khem. Zhur.*, 1934, **9**, 263; *Brit. Chem. Abs.* **B**, 1935, 258; *Chem. Abs.*, 1935, **29**, 6023.

[40] C. Candea and J. Kühn, *Chimie et industrie*, 1933, **29**, Special No., 861; *Brit. Chem. Abs.* **B**, 1933, 953; *Chem. Abs.*, 1934, **28**, 287.

[41] W. Hennicke, U. S. P. 1,931,492, Oct. 24, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 589.

[42] C. Candea and J. Kühn, *Petroleum Z.*, 1936, **32** (35), 11; *J. Inst. Pet. Tech.*, 1936, **22**, 500A; *Chem. Abs.*, 1936, **30**, 7513.

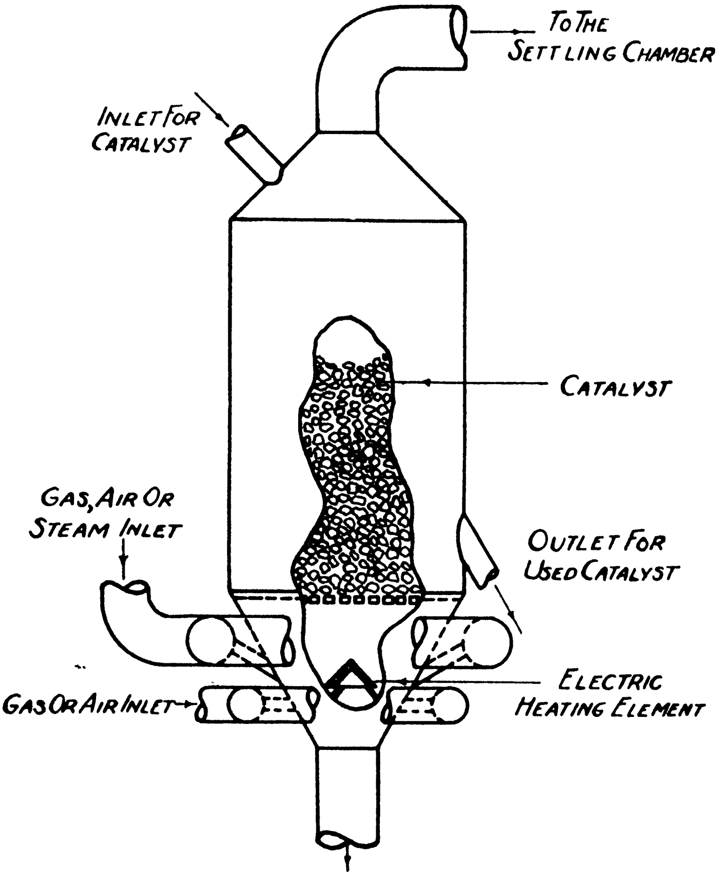

FIG. 73.—Drawing of Catalyst-packed Tower for Conversion of Carbon Monoxide to Dioxide and Carbon. (W. W. Odell)

High-melting compounds of metallic oxides of the iron group with acidic metal oxides of the 4th, 5th and 6th groups (e.g., the titanates, vanadates and tungstates of nickel, iron and cobalt) are employed in the decomposition of methane at temperatures above 800°C.[43] Other catalysts which have been suggested include the oxides of chromium, titanium, tungsten or molybdenum.[44]

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[43] German P. 616,976, 1935, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 583.

[44] E. Wilke and F. Fried, U. S. P. 2,042,285, May 26, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 5006. British P. 450,876, 1936; *Brit. Chem. Abs.* B, 1936, 968; *Chem. Abs.*, 1937, **31**, 228. French P. 796,010, 1936; *Chem. Abs.*, 1936, **30**, 7294. See also *Chrm. Trades J.*, 1936, **99**, 170; *J. Inst. Pet. Tech.*, 1936, **22**, 462A. French P. 796,010, 1936; *Chem. Abs.*, 1936, **30**, 7294.

The manufacture of carbon black from carbon monoxide is achieved by Odell[45] by conducting still gases and steam over a bed of solid fuel heated to 880°C. to yield carbon monoxide and hydrogen.

$$C_nH_{2n+2} + nH_2O = nCO + (2n + 1)H_2$$

The oxide is then converted to carbon and carbon dioxide by passing it rapidly through a tower packed with iron or a manganese-iron alloy at 500°C. (see Fig. 73). The gas and black leave the tower and pass to a settling chamber.

PETROLEUM COKE

The oldest method of preparing petroleum coke is by destructive distillation of heavy petroleum fractions in externally heated shell stills. The product from these coking stills is a hard brittle material with an oily luster and corresponding in composition to $C_{100}H_6$. It is one of the purest forms of industrial carbon, containing only a minute amount of ash, though coke prepared from Mexican oils contains some sulphur. The construction and operation of these stills in Russia has been described by Vuiborov,[46] who reports typical yields obtained in the coking of cracked residues. See Table 48.

TABLE 48.—*Yield from Russian Still.*

Coke	10-13%
Gas oil	75.5-82.3%
Gas and loss	7.5-12.2%
Fuel oil	7.0- 8.3%

Composition of Coke (in Per Cent)

Carbon	92.53-94.83
Moisture	1.0-1.4
Volatile matter	3.61-5.22
Ash	0.12-0.3
Iron	0.01
Silicon	0.04
Sulphur	0.39-0.48

The heterogeneous nature of the product resulting from coking petroleum oils has been noted by Simek,[47] who found that a mass of petroleum coke, 40-50 cm. thick, in the bottom of a still is divided into three main strata of which the center layer (the largest) is applicable for carbon electrodes. The lower layer, the crust, is porous, brittle, often graphitized, has a gray to silver gray color and contains some ash. The center and upper layers contain no ash and are black, relatively strong and somewhat elastic. The upper stratum, which is richest in volatile matter, is sufficiently soft to be cut, without crumbling, with a knife and is often returned to the next charge for further coking. It is reported by Simek that petroleum coke made in this way is almost inactive towards carbon dioxide at 1000°C., possibly in consequence of its very low ash content.

Since the advent of commercial cracking operations, the most important type of petroleum coke, from the point of view of quantity produced, is that obtained in cracking stills, where it is deposited in the soaking drum. This coke is very brittle and of honeycomb structure, although its composition depends largely on the type of oil employed and on the cracking conditions.[48] Variations in composition with the oil used are illustrated by Table 49.

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[45] W. W. Odell, U. S. P. 1,964,744, July 3, 1934; *Brit. Chem. Abs.* B, 1935, 982; *Chem. Abs.*, 1934, **28**, 5189. *Cf.* W. Oostveen, *Ind. chim. belge*, 1936, 7, 323; *Chem. Abs.*, 1936, **30**, 7792; *J. Inst. Pet. Tech.*, 1936, **22**, 463A.

[46] P. Vuiborov, *Azer. Neft. Khoz.*, 1933, 6-7, 29; *Chem. Abs.*, 1934, **28**, 7511.

[47] B. G. Simek, *Mitt. Kohlenforschungsinst. Prag*, 1933, 482; *Brit. Chem. Abs.* B, 1934, 228; *Chem. Abs.*, 1934, **28**, 2167.

TABLE 49.—*Yield of Petroleum Coke.*

	Yield in Per Cent		
Oil Employed	Fixed Carbon	Sulphur	Volatile
Kentucky..........	94.6	0.36	5.04
Arkansas...........	87.15	4.18	8.67

Petroleum coke is also made by the Knowles process,[49] which employs a wide, flat-bottom oven (see Fig. 74). The floor is heated from below by a series of narrow, parallel combustion chambers and is constructed of silicon carbide. A temperature of 980°C. is maintained during the first operation, which comprises continual pouring of petroleum residues into the oven until a thick layer of coke is formed.[49a] The temperature may then be raised to 1095°C. by further heating. The coke is usually hard and dense[50] and contains very little ash or volatile matter. A high grade material is manufactured in Germany by coking coal-tar pitch in cast-iron retorts. This pitch coke is reported to contain 0.5 per cent ash and the same amount of volatile materials and is preferred for electrode manufacture because of its regu-

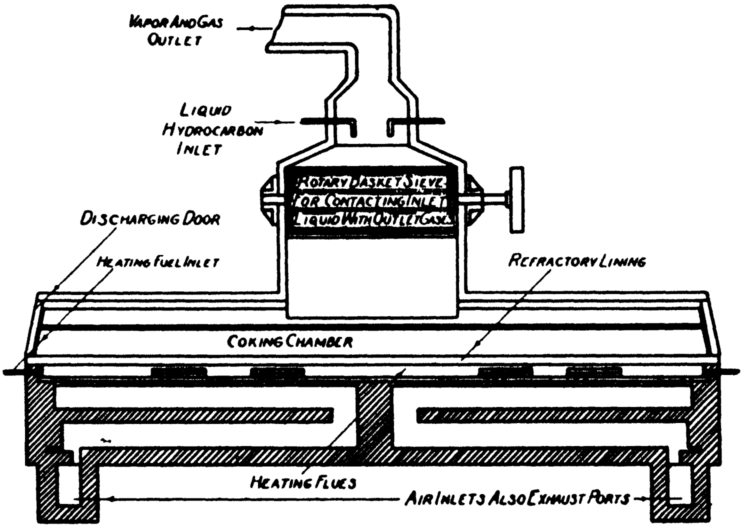

FIG. 74.—Sketch of One Form of Knowles Process Coking Oven. (A. S. Knowles and C. W. Andrews)

larity in quality. When operation is carried out under reduced pressure, yields of 50-60 per cent coke, 30-40 per cent oil and about 5 per cent resinous substances together with some gas and ammonia are obtained.

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[48] For a discussion of the structure and uses of petroleum and pitch coke, see *Engineering*, 1935, **139**, 585; *J. Inst. Pet. Tech.*, 1935, **21**, 303A.

[49] D. Brownlie, *Ind. Eng. Chem.*, 1936, **28**, 629; *Chem. Abs.*, 1936, **30**, 4647. See also A. L. Foster, *Nat. Pet. News*, 1936, **28** (19), 33; *J. Inst. Pet. Tech.*, 1936, **22**, 362A.

[49a] See A. S. Knowles and C. W. Andrews, U. S. P. 1,906,863 and 1,906,864, May 2, 1933, to Tar and Petroleum Process Co.; *Chem. Abs.*, 1933, **27**, 3591. U. S. P. 1,885,920, Nov. 1, 1932; *Chem. Abs.*, 1933, **27**, 1149. See also A. S. Knowles, U. S. P. 1,789,312, Jan. 20, 1931, to Tar and Petroleum Process Co.; *Chem. Abs.*, 1931, **25**, 1374.

[50] O. F. Campbell, *Oil & Gas J.*, 1935, **33** (45), 68; *J. Inst. Pet. Tech.*, 1935, **21**, 273A; *Chem. Abs.*, 1935, **29**, 4551.

Coking heavy oil stocks by passage of a hot gaseous medium through them is described by Vobach and Rogers.[51] For this purpose, the reaction vessel (see Fig. 75), which is conical with the larger end uppermost, is lined with a frangible material, such as fireclay and water-glass paste. The lining is fractured at the narrow end of the vessel by means of a hydraulic ram, so that the charge can be removed *en bloc*. Petroleum coke containing mineral matter evenly distributed throughout its mass was prepared by Duff[52] by carbonizing a mixture of petroleum and a mineral-bearing substance, such as coal or shale.

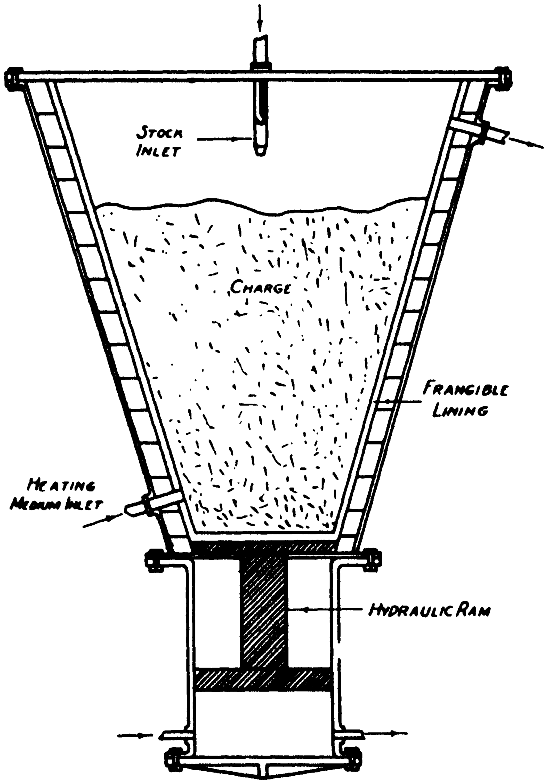

FIG. 75.—Coking Receptacle with Frangible Lining. (A. C. Vobach and H. K. Rogers)

Consumption of petroleum coke for the manufacture of carbon electrodes is increasing steadily, especially in Europe, where 120,000 tons are imported yearly for this purpose. Perhaps the most important use is as a fuel, for which purpose it is said to possess advantages over other solid fuels in that it gives less ash, needs less attention (owing to higher calorific value and consequent reduction in number of fillings) and shows improved sensitivity where thermostatic control is provided.[53] A carbonaceous fuel is prepared by Fisher[54] by mixing pulverized petroleum coke (the volatile matter of which has been previously reduced to 1 to 5 per cent by retorting) with a binder and briquetting the mixture, which may be carbonized afterwards.

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[51] A. C. Vobach and H. K. Rogers, U. S. P. 1,935,067, Nov. 14, 1933, to Sinclair Refining Co.; *Brit. Chem. Abs.* B, 1934, 821; *Chem. Abs.*, 1934, **28**, 631.

[52] W. Duff, British P. 410,881, 1934; *Chem. Abs.*, 1934, **28**, 7520; *Brit. Chem. Abs.* B, 1934, 746.

Petroleum coke has been used as a fuel for industrial boilers and furnaces, but it is not generally employed in metallurgical operations because of its poor mechanical strength and high sulphur content. However, coking still residues are said to compare favorably with coal cokes for foundry purposes except in regard to porosity, and may be used in the manufacture of all grades of iron.[55]

Activated Carbon. Several proposals have been made to produce activated carbon from petroleum coke. Oberle[56] suggests heating as high as 2000°C., under pressures of 50-500 lbs. per sq. in., and in the presence of steam, activating gases or salts, or mineral acids. Volatile reaction products are withdrawn during the treatment. Another method is to mix pulverized coke intimately with heated atomized mercury, or a low-melting alloy, and steam and pass the mixture through a "thermolizing" coil.[56a] The advantages are stated to be a very brief time of contact, good temperature control and prevention of clogging of the system. The activated carbon is recovered from the metal in a subsequent settling operation.

In a process of Faben[57] heavy petroleum residues are destructively distilled by contact with hot combustion gases. The flow of the latter is regulated so that the temperature does not exceed 700°C., and is continued until a coke of low volatile content is produced. This coke is converted into activated carbon by heating to about 900°C. in an oxidizing atmosphere, e.g., superheated steam. Another method consists in digesting petroleum coke with certain reagents (unspecified) in a closed container for 1 hour at 300°F. and for an hour at 800°F.[58] After cooling, washing with water, with an acid solution of 50 per cent strength and then twice with water, it is finally dried with exhaust steam. The yield of coke is 40-60 per cent of the raw material and its ash content is 1 per cent.

Mótusz[59] has reported an interesting sidelight on the use of activated carbon. Four types, Carbonit-Frankfurt, Eponit-Ratibor, Charbon activ-Paris, and Carbo-Merck were employed to clarify wines and the increase in ash content of the liquid noted. He found that the amounts of ash in these carbons (17.64, 11.13, 11.49 and 1.78 per cent, respectively) rendered them unsuitable for such purposes, and recommended an active carbon whose ash content was less than 1 per cent.

The graphitization of petroleum coke is described by Derby.[60] He passes the coke through a vertical furnace where it is progressively heated by surface combustion to 1800°C. (see Fig. 76). A coreless electric induction furnace, which forms part of the apparatus, then raises the temperature to 2500°C.

[53] O. F. Campbell, *loc. cit.*

[54] A. Fisher, U. S. P. 1,916,306, July 4, 1933, to Universal Oil Products Co.; *Brit. Chem. Abs.* B, 1934, 487; *Chem. Abs.*, 1933, 27, 4654.

[55] C. B. Carpenter, *Mech. Eng.*, 1934, 56, 330; *Chem. Abs.*, 1934, 28, 4864. See also D. G. Jones, *Refiner Natural Gasoline Mfr.*, 1936, 15, 280; *J. Inst. Pet. Tech.*, 1936, 22, 464A.

[56] A. Oberle, U. S. P. 1,903,834, April 18, 1933; *Brit. Chem. Abs.* B, 1933, 1044; *Chem. Abs.*, 1933, 27, 3300.

[56a] A. Oberle, U. S. P. 2,015,085, Sept. 24, 1935; *Chem. Abs.*, 1935, 29, 7621; *Brit. Chem. Abs.* B, 1936, 679.

[57] C. R. Faben, U. S. P. 1,925,438, Sept. 5, 1933; *Brit. Chem. Abs.* B, 1934, 663; *Chem. Abs.*, 1933, 27, 5491.

[58] A. L. Nugey, *Refiner*, 1934, 13, 49; *J. Inst. Pet. Tech.*, 1934, 20, 253A; *Chem. Abs.*, 1934, 28, 2168.

[59] J. Mótusz, *Kisérletügyi Közlemények*, 1935, 38, 169; *Chem. Abs.*, 1936, 30, 1954.

[60] I. H. Derby, U. S. P. 1,975,259, Oct. 2, 1934, to P. C. Reilly; *Brit. Chem. Abs.* B, 1935, 936; *Chem. Abs.*, 1934, 28, 7442.

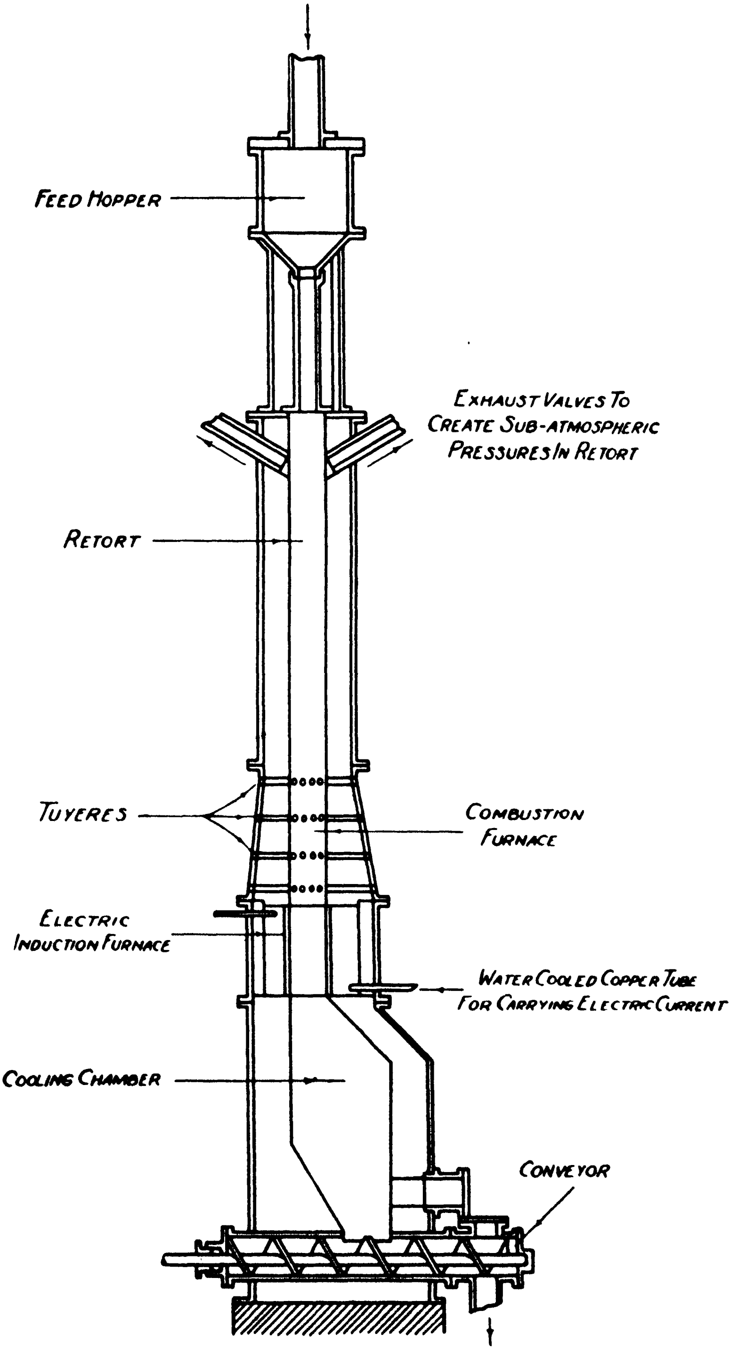
Feed Hopper
Exhaust Valves To Create Sub-atmospheric Pressures In Retort
Retort
Tuyeres
Combustion Furnace
Electric Induction Furnace
Water Cooled Copper Tube For Carrying Electric Current
Cooling Chamber
Conveyor

Fig. 76.—Furnace for Graphitizing Petroleum Coke. (I. H. Derby)

PURIFICATION OF HYDROGEN

The hydrogen produced by simple thermal decomposition of methane (or its homologues) always contains small amounts of that hydrocarbon and its removal is a matter of technical importance where very pure hydrogen is desired. Because of its inactivity chemical methods of separation are not readily applicable. Of the physical methods, preferential solvent action is usually advocated, although absorption of methane is also possible. According to Karzhavin and Gerchikova,[61] the solubility of methane in low-boiling benzine is sufficient to warrant the use of the latter with hydrogen-nitrogen mixtures, but the washing operation should be carried out at high pressures and low temperatures. Kerosene and heavier oils are not satisfactory for this purpose.

Carbon monoxide, which is usually present in the hydrogen produced by partial combustion of methane with steam, oxygen or air, is an undesirable constituent for many purposes. The extreme solubility of carbon monoxide in ammoniacal cuprous salt solutions has been utilized on an industrial scale for the removal of small amounts from hydrogen-nitrogen mixtures employed in the synthesis of ammonia. It has been found by Zhavoronkov and Reshchikov[62] that ammoniacal solutions of cuprous formate and lactate are superior to those of the chloride and acetate. Cuprous ammonium formate absorbs carbon monoxide more readily than the lactate but the solution is less stable and regeneration more difficult. To prevent the separation of free copper, cupric salts should be present in the solution to the extent of at least 20 grams of divalent copper per liter. Absorption is best carried out at 0-20°C., and regeneration of the solution should take place at 70-80°C. and at atmospheric, or subatmospheric, pressure.

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[61] V. A. Karzhavin and S. Yu. Gerchikova, *J. Chem. Ind. (Moscow)*, 1933, No. 7, 26; *Chem. Abs.*, 1934, **28**, 1117; *Brit. Chem. Abs.* **B**, 1934, 6.

[62] N. M. Zhavoronkov and P. M. Reshchikov, *J. Chem. Ind (Moscow)*, 1933, No. 8, 41; *Chem. Abs.*, 1934, **28**, 1474; *Brit. Chem. Abs.* **A**, 1934, 139.

Chapter 8

The Carbon Black Industry. Deposition of Carbon from Flames

Carbon black is essentially pure carbon in an exceedingly fine state of subdivision. It is obtained by incomplete combustion of hydrocarbons in a limited amount of air, and its properties and qualities are greatly influenced by relatively minor alterations in the mode of operation. The so-called gas blacks are the most important, not only in quantity produced but also in quality.

In the case of gas blacks, carbon resulting from the incomplete combustion of the hydrocarbon gas is deposited on cooled surfaces on which the flames are allowed to impinge. The channel, rotating disk, plate and roller methods are all variations of this principle. The channel process is by far the most important of these methods, being responsible for about 90 per cent of the carbon black produced in America.[1] In the case of Fumarex and similar types of carbon black, no precipitating surface is used, the hot gaseous products being passed into settling chambers where the finely divided carbon is removed by filtration or by washing with water. Lampblacks are obtained by a similar process in which liquid and solid hydrocarbons are burnt in a limited air supply without the use of precipitating surfaces.

Another type of carbon is made by the thermal decomposition of hydrocarbons under carefully controlled conditions either in continuous or batch operation. The principles underlying this mode of production of carbon blacks, which include the Thermax and P.33 products of the Thermatomic Carbon Co., are discussed in Chapter 7. Materials, such as petroleum coke, obtained by destructive distillation of organic substances may also be classed under this heading although they bear no relation to carbon blacks in general.

Certain types of black have been produced by exploding a hydrocarbon gas, such as acetylene, in a limited supply of air. Another procedure consists in decomposing hydrocarbon gas or vapors (and also liquid hydrocarbons) by an electric discharge.[2] No information is available as to the extent to which such methods have been, or are being, exploited industrially.[3]

The manufacture of carbon black is confined almost exclusively to the U.S.A., although small quantities are now being made in Canada, Germany, Rumania, Japan, Russia and a few other countries for domestic use. The annual productions of carbon black in the U.S.A., as well as the annual sales, both domestic and for export, for the years 1928-1935 inclusive are listed[4] in Table 50, which shows very clearly the wide-spread use of the channel process.

According to Drogin,[5] 350 million lbs. of black were made in the U.S.A. in 1935, of which 310 million lbs. were prepared by the channel process. The domestic

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[1] G. Ewald, *Brennstoff-Chem.*, 1936, 17, 41; *Brit. Chem. Abs.* **B**, 1936, 354; *Chem. Abs.*, 1936, **30**, 6142.

[2] For a discussion of such methods, see Chapters 7 and 9.

[3] For a review of the development of carbon black manufacture in North America, see W. Esch, *Kautschuk*, 1933, **9**, 104; *Chem. Abs.*, 1933, **27**, 4883.

[4] G. R. Hopkins and H. Backus, Minerals Yearbook (U. S. Bur. Mines), **1936**, 762.

[5] I. Drogin, *Chem. Met. Eng.*, 1936, **43**, 95; *Chem. Abs.*, 1936, **30**, 3174.

TABLE 50.—*Production of Carbon Black in the United States.*

Year	1928	1929	1930	1931	1932	1933	1934	1935
Number of producers reported	31	35	33	26	24	25	25	21
Number of plants	65	71	69	58	50	51	50	54
Production (thousands of pounds)								
By Channel process	220,532	327,552	350,254	255,322	224,536	238,026	293,546	316,284
By other processes	28,258	38,890	29,688	25,585	18,164	35,099	35,282	36,465
Total	248,790	366,442	379,942	280,907	242,700	273,125	328,828	352,749
Quantity sold (thousands of pounds)								
Domestic								
To rubber companies	140,938	138,474	128,572	134,315	130,380	191,358	165,446	213,708
To ink companies	27,223	27,350	19,220	15,184	18,341	18,539	16,146	15,177
To paint companies	20,040	17,257	11,922	6,760	7,636	6,260	5,365	6,550
For miscellaneous purposes	14,475	8,896	7,565	5,453	5,126	6,025	5,035	9,916
Exported	77,903	91,829	84,260	96,714	100,072	152,286	120,620	142,185
Total	280,579	283,806	251,539	258,426	261,555	374,468	312,612	387,536

consumption in 1935 included 182 million lbs. in the rubber industry and 17 million lbs. in the printing ink industry, the average price being 4 to 8 cents per lb. with a maximum price of $1.10 per lb. for certain jet blacks. Approximately 35 per cent of all carbon black sold in the U.S.A. is exported, the principal consuming countries being Great Britain, France and Germany.

The main producing areas of the U.S.A. are at present located in the states of Texas, Louisiana, Oklahoma and Wyoming. Of these, the Panhandle district of Texas is by far the most important, about 76 per cent of the total world production being manufactured in that region alone.

DEPOSITION OF CARBON BLACK FROM NATURAL GAS FLAMES BY USE OF COOLING SURFACES

Despite numerous attempts to develop more economical methods of manufacture, the incomplete combustion of natural gas and deposition of the resulting carbon on suitable cooling surfaces still remains by far the most important method of operation.[6] From a chemical point of view the yields obtained, which average 1.43 lbs. per 1000 cu. ft. of natural gas burned or about 4 per cent of the theoretical,[6a] are far from satisfactory but are justified by the high quality of the product and the cheapness of the raw material. In 1935 the price of natural gas employed in gas black manufacture was about 3 cents per 1000 cu. ft.[7]

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[6] Reviews of carbon black production have been given by Carleton Ellis, *Petroleum Z.*, 1935, **31** (14), 9; *Chem. Abs.*, 1935, **29**, 7595. I. Drogin, *India Rubber J.*, 1935, **90**, 259; *Chem. Abs.*, 1935, **29**, 8249; *Brit. Chem. Abs.* B, 1935, 932. E. Dittrich, *Brennstoff-Chem.*, 1935, **16**, 121; *J. Inst. Pet. Tech.*, 1935, **21**, 210A; *Chem. Abs.*, 1935, **29**, 5631; *Brit. Chem. Abs.* B, 1935, 534. N. Pirozhkov, *J. Rubber Ind. (U.S.S.R.)*, **1936**, 594; *Chem. Abs.*, 1936, **30**, 6900. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[6a] Assuming that the natural gas is entirely methane and that volumes are measured at N.T.P., 1000 cu. ft. of gas should theoretically yield about 33.4 lb. of carbon black.

[7] I. Drogin, *Chem. Met. Eng.*, 1936, **43**, 95; *Chem. Abs.*, 1936, **30**, 3174.

The factors influencing the choice of natural gas are (1) nitrogen content, (2) sulphur content, (3) natural gasoline content, (4) gas pressure, (5) proximity of gas wells to carbon black plant, and (6) industrial and domestic demand for the gas.[8] Nitrogen in high concentrations enormously reduces the yield, a gas of 41.3 per cent nitrogen giving only 0.068 lbs. of black per 1000 cu. ft. Gas containing more than 1.5 grains of hydrogen sulphide (approximately 0.007 per cent by volume), or 30 grains total sulphur per 100 cu. ft. is regarded as dangerous, because of its corrosive action on the burner pipes, although Pidgeon[9] believes that concentrations as high as 1 per cent of hydrogen sulphide have but little effect on the yield and properties of black. Natural gasoline affects the quality, and it has been found more profitable to extract the gasoline rather than to burn it for the production of black.

Pidgeon[9a] points out that although low prices for carbon black result as long as the natural gas supply exceeds the demand, this condition will not always remain so, and eventually more economical means of production must be found. One suggested outlet is the utilization of waste gases from cracking operations since it has appeared that olefins are largely responsible for carbon black formation in pyrolysis operations. Using an experimental channel plant, it was shown that the amount of black obtained from a given volume of propane-butane mixture was greater if the gas was first pyrolyzed (up to 850°C.) to yield aromatic liquids and the residual gases burned, than if the original mixture was burned directly. Thus, the best yield obtained with the untreated paraffin mixture was 4.9 lb. per 1000 cu. ft., whereas the same gas after treatment produced 5.4 lb. per 1000 cu. ft. (of original gas) in addition to about 23 to 25 lb. of light oil formed during pyrolysis.

THE CHANNEL PROCESS

Details of the construction and operation of plants for the manufacture of carbon black by the channel process have been supplied by Allen, Price and Reinbold.[10] In this process, natural gas is burnt with a controlled deficiency of air in burners provided with lava tips of various types. The flame is projected against the underside of standard steel channels, 7 or 8 inches wide, in which the black is collected. The channels are bolted together forming a grid with the channel edges turned up. The grid is suspended by means of cross channels at the ends of which are fitted angles bearing flanged wheels which run on a track and carry the channel grid. The latter is moved continuously in a longitudinal direction with a reciprocating motion over the stationary gas flames. The deposited black is removed from the channels by scrapers and then falls into hoppers from which it is continuously removed by a screw conveyor (or other means) and transported to the bolting and packing houses. The whole arrangement of burners and channels is enclosed in burning houses, usually called hot houses, which are placed in rows 15-20 feet apart, this space or alley being reserved for the conveyors employed for transporting the product to the central packing house. Factories are now in operation with as many as 60 hot houses (operating continuously) per single packing house.

On reaching the packing house, the black is bolted, or sifted, in various ways to eliminate foreign matter and break up the flakes formed on the channels. It is next conveyed to a large bin where the volume-weight relationship is reduced to such a degree that it can be packed in paper bags by a standard screw packer. Handling of the material in bulk has been greatly facilitated by later developments whereby the black is treated in such a way as to give granular pellets of a size passing through a 20-mesh screen but retained by screens of 65-100 mesh. These pellets are agglomerated by special treatment so that the particles adhere firmly to one another and can be handled with very little formation of dust.[11] Moreover, this so-called dustless black has the same apparent density as the hydraulically, or mechanically, compressed product, and is chiefly used in rubber production. It is said that compression of carbon black eliminates practically all danger of fire during handling.

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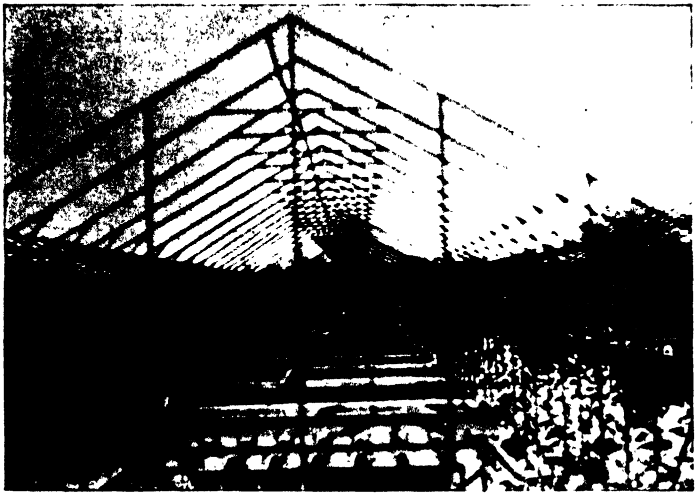
[8] *Chem. Trade J.*, 1936, **98**, 323; *J. Inst. Pet. Tech.*, 1936, **22**, 365A.

[9] L. M. Pidgeon, *Can. J. Research*, 1936, **14B**, 127; *Chem. Abs.*, 1936, **30**, 5373; *Brit. Chem. Abs.* **B**, 1936, 724.

[9a] L. M. Pidgeon, *Can. J. Research*, 1937, 15B, 67.

[10] R. G. Allen, H. W. Price and E. B. Reinbold, *Refiner*, 1935, **14**, 384; *Chem. Abs.* 1935, **29**, 8249.



Courtesy Columbian Carbon Co.

FIG. 77.—Channel Black Plant Under Construction.

Importance of the Flame in the Channel Process. According to Wiegand,[12] the draft conditions in the burner houses need to be adjusted frequently with change of wind and other atmospheric conditions. A good indication of conditions in the house is obtained by observation of the so-called "smoke blanket," which is a blackish haze appearing approximately at the level of the channel irons. If the smoke blanket rises above or falls below its normal level, an adjustment of drafts becomes necessary. The quality of the black has been shown to depend markedly on the type of flame used. Wiegand has stated that a flat flame is essential for a good product, while a round flame furnishes a gray form of black which is not satisfactory for most purposes. (The latter appears to develop at lower temperatures.) For obtaining a flat flame, the bat wing burner, which is slotted, or the fish-tail burner, which has two opposing jets, may be used. Tests made with rubbers compounded with 40 per cent of blacks made with a flat flame and a round flame, respectively, and with diphenylguanidine as accelerator, gave the following results:

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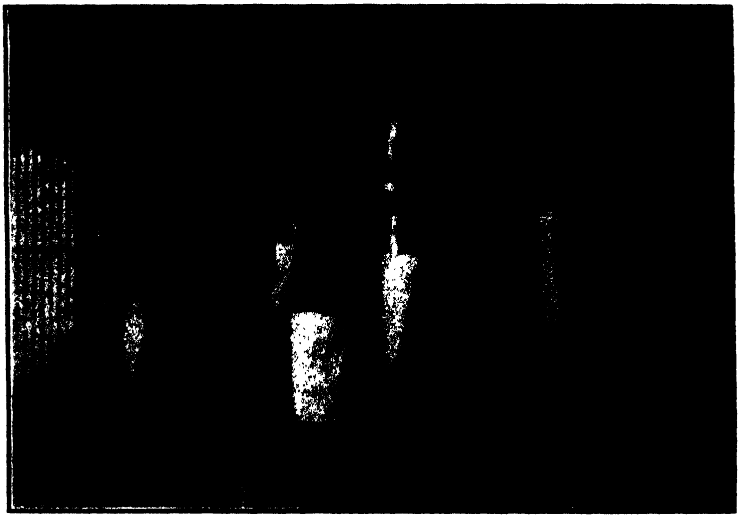
[11] A discussion of dustless blacks and the modification of the physical characteristics of blacks will be given later in this chapter.

[12] W. B. Wiegand. *Ind. Eng. Chem.*, 1931, **23**, 178; *Chem. Abs.*, 1931, **25**, 3442.

	Tensile Strength Lbs. per sq. in.	Elongation %
Black from round flame....	3800	580
Black from flat flame......	4700	630

Small scale experiments, described by Wiegand, indicate that the yield of carbon black depends not only on the flame structure but also on the channel height and the rate of flow of gas to the burners. The yields of carbon black obtained from round flames are greatly influenced by relatively slight changes in gas flow, whereas the flat type of flame is hardly affected over a considerable range of gas velocities. A flat flame is, however, more sensitive to channel height than the round flame.



Courtesy Columbian Carbon Co.

FIG. 77a.—Packaging Carbon Black.

Additional factors which have to be taken into account in large scale operation include size and shape of burning house, total gas to be burned in relation to size of house and channel area; spacing, width and reciprocating speed of channels and spacing, angle and accuracy of tip orifices.

Channel height is considered by Pidgeon[12a] to be the most important single variable affecting the properties of channel black. Proper adjustment of this height is essential because rather sharp maxima exist for both yield and quality. The greatest yield obtained in an experimental plant under constant flame conditions, i.e., size of burner tip and gas pressure, resulted with channel settings about intermediate between the lowest height tolerated by the flame and the highest at which any carbon recovery was possible. An approximately straight-line relationship existed between yield and quality, based on the rubber-reinforcing properties of the product. It was suggested that changes in quality of carbon black

[12a] L. M. Pidgeon, *Can. J. Research*, 1937, 15B, 187.

from any one plant may be the result of variations in effective channel height brought about by fluctuations in gas pressure and atmospheric conditions.

Other Surface Impingement Processes. Lewis[13] impinges the hydrocarbon flame on a metallic surface maintained at a high temperature. Radiation from this depository is checked by covering the unproductive areas of the plate with a layer of insulating material. Fireclay, asbestos and ceramic cement are all recommended for this purpose.

According to Guyer,[14] gases obtained in oil cracking, rich in propane and butane, may be subjected to further controlled partial cracking at 675-950°C. and at a contact time of 0.002 to 0.02 minutes to produce olefins. These gases, containing 35 to 50 per cent of unsaturated hydrocarbons, may be decomposed by partial combustion.

PRODUCTION OF BLACKS BY NON-IMPINGEMENT PROCESSES

The incomplete combustion of gaseous, liquid or solid hydrocarbons may be controlled to furnish lampblack, a species of carbon black having properties somewhat different from those of the normal gas blacks. In processes of this sort in which flame impingement on solid surfaces is not employed, the hydrocarbons are burnt with a deficiency of air in flames and the gaseous products of combustion entrain the carbon formed, which is recovered by filtration or water-washing.[15]

In the Lewis process,[16] a product known as Fumarex is produced by the incomplete combustion of natural gas in firebrick-lined furnaces. The mass of flame, which is about 8 feet across, is varied in height according to the grade of black required, the combustion being gauged by the appearance of the heavy blanket of fumes. On leaving the top of the furnace, the fumes pass through a horizontal pipe into the collectors where they are washed by a countercurrent spray of water. By this means, the gas is cooled and simultaneously freed from the finely divided carbon particles which remain suspended in the water and pass with it to large settling tanks provided with conical bottoms to facilitate deposition and removal of the very heavy slurry of carbon black and water. The slurry is passed through a filter press and dried. Fumarex possesses characteristics quite different from those of channel or gas blacks. It is not as black in toptone or in tinctorial power but is much softer and has a clear blue undertone. One of its main uses is in the manufacture of soft rubber goods, such as shoes or hose.[11]

Pidgeon[18] has described a method whereby hydrocarbon gases, such as propane-methane or ethane-propane are thermally decomposed to give yields as high as 60 per cent of the available carbon in the feed by employing a "wall-free" reaction space. A porous refractory tube through which an inert gas may be passed serves for this purpose. The advantage of this type of apparatus is that the reacting gas is unable to come in contact with the walls of the system, so that the deposition of carbon thereon is prevented, and at the same time, an efficient heat transfer between the source of heat and the reacting gases is maintained. The tube was heated to 1300-1400°C. in a gas fired furnace and the rate of diffusion of the inert gas was controlled by varying the pressure difference across the walls of the tube. The black produced in this manner is said to be similar to those of the "soft" type in that it has a high density, low sorptive power, imparts similar resistance to aging and abrasion and accelerates the cure in a rubber stock.

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[13] G. C. Lewis, U. S. P. 1,944,715, Jan. 23, 1934, to Columbian Carbon Co.; *Chem. Abs.*, 1934, **28**, 2137; *Brit. Chem. Abs.* B, 1934, 998.

[14] J. A. Guyer, U. S. P. 1,946,739, Feb. 13, 1934, to Phillips Petroleum Co.; *Chem. Abs.*, 1934, **28**, 2479.

[15] Investigation has shown that the decomposition is not as simple as outlined by the reaction $CH_4 \rightarrow C + 2H_2$. G. C. Lewis (private communication) reports the formation of naphthenes, nitrobenzene, and cyanogen compounds in varying amounts, from natural gas. A. W. Campbell, N. H. Cromwell and J. J. Hager (*J.A.C.S.*, 1936, **58**, 1051; *Brit. Chem. Abs.* B, 1936, 774; *Chem. Abs.*, 1936, **30**, 5215) have identified acenaphthylene and pyrene in the organic matter produced in the Thermatomic process. (See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., 1934, 210, for a description of this method.)

[16] G. C. Lewis, U. S. P. 1,801,436, April 21, 1931, to Columbian Carbon Co.; *Chem. Abs.*, 1931, **25**, 3447; *Brit. Chem. Abs.* B, 1932, 8.

[17] Private communication from G. C. Lewis.

[18] L. M. Pidgeon, *Can. J. Research*, 1935, **13B**, 351; *Chem. Abs.*, 1936, **30**, 1953; *Brit. Chem. Abs.* B, 1936, 225.

Keller produces carbon black by causing parallel streams of air and gaseous hydrocarbons to flow upward in sheets of one-eighth to one-half inch thickness within a heated unobstructed space, protected from atmospheric disturbances, under such conditions that adjacent streams of gas and air come into contact while maintaining streamline flow. The amount of air used is from 55 to 80 per cent of that required for combustion of the gas. The ratio of the velocities of the gas and air streams is maintained between 1 :0.67 and 1 :2 and the absolute velocities are such that the carbon black, which is formed at the surface of contact, remains in the high temperature zone for 0.05-0.4 second.[19]

Courtesy G. C. Lewis

FIG. 78.—Plant for Manufacture of Carbon Black by Lewis Wet Process.

Prerau recommends preheating the hydrocarbon material and burning it in open furnaces in a blast of heated air or a mixture of air and gases,[20] and Kingo reports increased yield and better quality by automatically introducing cold air into the flue connecting the condensation chamber with the collecting chamber.[21] Dissociation of hydrocarbons by passage through a layer of live flame at a temperature of 1000-1400°C. has also been proposed.[22] Heid[23] suggests intimately mixing vaporized oil with hot combustion products whereby partial cracking takes place. The gaseous mixture, together with any entrained carbon is removed from the reaction zone and subjected to incomplete combustion.

Hydrocarbons such as ethylene, propane and butane, not explosive by themselves, can be decomposed by ignition of explosive mixtures of the gas with oxygen.[24] The amount of oxygen used should be just sufficient to form the necessary explosive mixture, as an excess will result in complete combustion to gaseous products. The black obtained is particularly suited as a filler for rubber. Acetylene-oxygen mixtures may also be treated in this manner.[25] Mixing steam with the gas and oxygen has also been advocated to give, in addition to carbon black, an exit gas having a composition of hydrogen and carbon monoxide suitable for a feed stock for subsequent conversion into ammonia or methanol.[26]

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[19] T. P. Keller, U. S. P. 1,999,541, Apr. 30, 1935, to Doherty Research Co.; *Brit. Chem. Abs.* B, 1936, 485; *Chem. Abs.*, 1935, **29**, 4140.

[20] I. Prerau, Hungarian P. 113,300, 1935; *Chem. Abs.*, 1936, **30**, 2718.

[21] T. Kingo, Japanese P. 110,776, 1935; *Chem. Abs.*, 1936, **30**, 2335.

[22] R. H. Brownlee, Canadian P. 355,517, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 217. Also British P. 402,322, 1933 to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 3196; *Brit. Chem. Abs.* B, 1934, 181. French P. 754,767, 1933; *Chem. Abs.*, 1934, **28**, 1483.

[23] J. B. Heid, U. S. P. 1,986,198, Jan. 1, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 1219; *Brit. Chem. Abs.* B, 1935, 1033.

ACETYLENE BLACKS

Acetylene is used quite extensively for the manufacture of carbon blacks abroad. One of the methods in use at present is based upon the fact that acetylene subjected to a pressure of more than two atmospheres will propagate decomposition throughout the total volume if this is started in one place by an electric spark or other means. Both carbon and hydrogen are recovered in this process and the black resulting is known as acetylene explosion black. It is finely divided and a very pure carbon, but the intensity of color is less than that of the channel carbon.[27]

A purely thermic process of decomposing acetylene has been developed in Canada. Acetylene is dissociated into its elements by heating to the decomposition temperature (800°C.). The black produced is not of an intense nature, but due to its very voluminous properties, it possesses several other extremely valuable characteristics, such as high mechanical absorption, small particle size and a relatively high electrical conductivity.[28]

PRODUCTION OF BLACKS FROM LIQUID AND SOLID HYDROCARBONS

The manufacture of lampblack has been carried out for many years by the incomplete combustion of cheap raw materials, such as creosote, naphthalene or tar oils, the smoky vapors being cooled and treated for the removal of the suspended particles. In general, lampblacks so prepared have physical characteristics markedly different from those of carbon black and cannot compete with the latter in most of its major applications. However, certain types of carbon black adapted for special uses may be produced by burning hydrocarbon oils under controlled conditions though it is doubtful whether truly high grade products can be made in this way. In Russia, black is being manufactured by the incomplete combustion of green oils,[29] the gaseous products being cooled to 50-70°C. and filtered. A material prepared in this way contained 0.38 per cent moisture, 0.04 per cent ash, 1.76 per cent volatile material, and had a volume of 7.28 cc. per gram.[30]

An apparatus somewhat reminiscent of that employed in the well-known channel process is used by Dusek.[31] The fuel (such as naphthalene) is fed to parallel rows of orifices in a multiflame flat burner, directly under a grate-shaped cooler

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[24] I. G. Farbenind. A.-G., French P. 795,048, 1936; *Chem. Abs.*, 1936, **30**, 5376.

[25] French P. 799,354, 1936 to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 7796.

[26] R. S. Richardson, U. S. P. 2,013,699, Oct. 10, 1935, to Chemical Construction Corp.; *Brit. Chem. Abs.* **B**, 1936, 932; *Chem. Abs.*, 1935, **29**, 7029.

[27] C. Kaufmann, *Chem. Markets*, 1933, **33**, 217; *Can. Chem. Met.*, 1933, 17, 93; *Chem. Abs.*, 1933, **27**, 3782.

[28] C. Kaufmann, *loc. cit.*

[29] Green oil is a fraction obtained in the redistillation of crude bituminous shale oil, and has a sp. gr. 0.858. After refining with sulphuric acid it gives, on further fractionation, 31 per cent burning oil, 13 per cent lighting oil, 11 per cent middle oil and 15 per cent paraffins. (E. Molinari, "Treatise on General and Industrial Organic Chemistry," P. Blakiston's Son and Co., Philadelphia, 1913, 84).

[30] G. Dubrovin, *J. Rubber Ind. U.S.S.R.*, 1935, **12**, 257; *Chem. Abs.*, 1935, **29**, 6372. P. V. Chernyak, *J. Rubber Ind., U.S.S.R.*, 1935, **12**, 165; *Chem. Abs.*, 1935, **29**, 6372. S. Grigorov (*J. Rubber Ind., U.S.S.R.*, **1936**, 179; *Chem. Abs.*, 1936, **30**, 6542) has described a process for obtaining green oil for the production of lampblack.

[31] J. Dusek, British P. 434,393, 1935; *Brit. Chem. Abs.* **B**, 1935, 1082; *J. Inst. Pet. Tech.*, 1935, **21**, 421A; *Chem. Abs.*, 1935, **29**, 8256.

Fig. 79.
Thermal Acetylene Black.

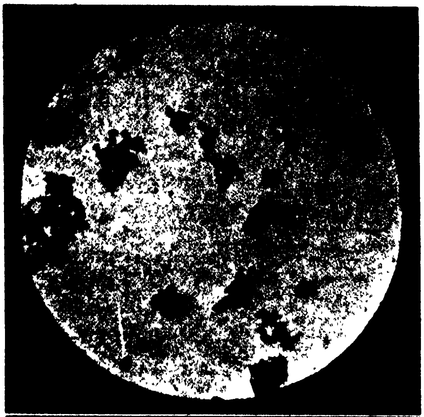


Fig. 80.
Explosion Acetylene Black.

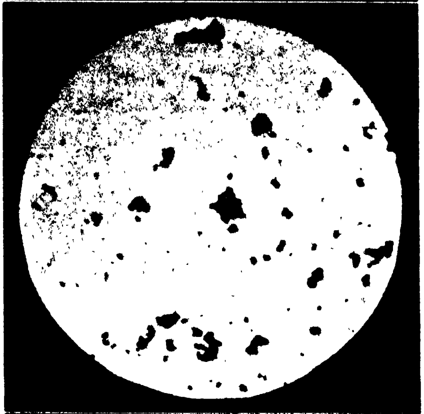
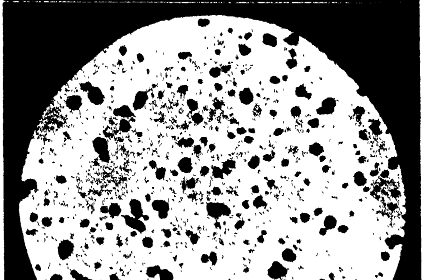


Fig. 81.
Channel Acetylene Black.



Courtesy Chemical Industries

Figs. 79-81.—Photomicrographs of Acetylene Blacks. Enlargement 1000 Diameters.
(C. Kaufmann)

made up of parallel water-cooled tubes approximately twice the length of the burner and capable of being moved periodically to and fro through the flame. The carbon deposits on the tube-surface and is automatically brushed into the collecting receptacles arranged on either side of the burner. Jakosky[32] has suggested converting solid material, e.g., still residues, gilsonite, or copal resin, into blacks. In his procedure, the material is treated with a solvent (e.g., Diesel oil or alcohol), and after separation from the impurities the solution is subjected to localized high-temperature heating to effect dissociation. Morrell[33] has proposed to carbonize a mixture of finely divided carbonaceous material and an aqueous emulsion of wood- or coal-tar pitch.

PHYSICAL AND CHEMICAL PROPERTIES

The physical and chemical properties of carbon blacks vary considerably, depending upon the processing and type of hydrocarbon gas used. Kaufmann[34] gives a comparison of the properties of acetylene black obtained by the thermal, explosion and channel methods. (See Table 51.) While the channel acetylene blacks are related to the American gas blacks, the thermal acetylene blacks resemble high grade lampblacks, but owing to the high temperature of formation, the properties of these thermal blacks approach those of finely divided graphite.

TABLE 51.—*Comparison of Properties of Carbon Blacks.*

		Acetylene Blacks	
	Thermal	Explosion	Channel
True density	2.05	1.89	——
Resistivity at 2500 lbs./sq. in. pressure, ohms/sq. in.	0.0464-0.035	0.0624-0.0564	0.2180-0.1400
Tinting value (nigrometer)	100	130	140
Microstructure	Loose, spongy structure	Loose, spongy structure	Dense, solid bodies
Absorption of linseed oil, grams/gram of black	5	3.7	2.18
Wetability	None	None	Readily

The purity of the acetylene blacks is quite high, seldom less than 95 per cent.[35] The impurities are usually polymerization products of acetylene, principally aromatics such as benzene, naphthalene, anthracene or phenanthrene (especially in the case of the low-temperature operations), or mechanically introduced substances such as iron[36] or silica. See Table 52.

TABLE 52.—*Impurities in Acetylene Blacks* (*Values given are in per cent*)

Type	Moisture	Volatile	Ether Extract	Ash
Thermic	0.05	1.3	0.02	0.04
Explosion	0.06	1.0	0.05	0.03
Channel	0.38	3.0	0.6	1.0

Day and co-workers[37] have investigated the ash obtained upon combustion of blacks produced from various hydrocarbons. The ashes obtained were white, partially soluble in hydrochloric acid and completely soluble in hydrofluoric acid. Ash values (in per cent) obtained with liquid hydrocarbons are:

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[32] J. J. Jakosky, U. S. P. 2,054,084, Sept. 15, 1936, to Electroblacks, Inc.; *Chem. Abs.*, 1936, 30, 7796.

[33] J. C. Morrell, British P. 445,342, 1936, *Brit. Chem. Abs.* B, 1936, 628; *Chem. Abs.*, 1936, **30**, 6518; British P. 446,889 and 446,892, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 323A; *Brit. Chem. Abs.* B, 1936, 729.

[34] C. Kaufmann, *Chem. Markets*, 1933, **33**, 217; *Can. Chem. Met.*, 1933, 17, 93; *Chem. Abs.*, 1933, 27, 3782.

[35] C. Kaufmann, *loc. cit.*

[36] Iron may be removed by treatment with chlorine or hydrogen chloride at 400° C. or higher. See British P. 456,252, 1936, to Bayerische Stickstoff-Werke A.-G.; *Brit. Chem. Abs.* B, 1937, 13.

[37] J. E. Day *et al.*, *Ind. Eng Chem.*, 1936, **28**, 234; *Chem. Abs.*, 1936, **30**, 1954.

Benzene	0.023	Turpentine	0.027
Toluene	0.133	Kerosene	0.032
Xylene	0.123		

Unpurified acetylene and natural gas resulted in blacks with an ash content of about 0.5 per cent, whereas values as low as 0.01 per cent were obtained using acetylene of a better quality.

A carbon black, Carbomet No. 3, made from Transylvania natural gas, has been found to be satisfactory for rubber compounding. Waldner[38] believed this Rumanian black is equal, and in some respects even superior, to American gas blacks. Table 53 gives comparative values for the Rumanian product and Dixie Ordinary, an American gas black.

TABLE 53.—*Properties of American and Rumanian Gas Blacks.*

	Carbomet No. 3	Dixie Ordinary
Apparent sp. gr.	0.160	0.110
True sp. gr.	1.78	1.76
Fineness (in Chancel degrees)[a]	20	20
Coloring power	Good	Good
Acetone extract	0.3	0.26
Ash	0.058	0.073
Oil absorption, cc./100 g.	230	250
Iodine adsorption, mg/100 g.	257	274
Methylene blue adsorption, mg./100 g.	49.54	43.60
Diphenylguanidine adsorption	18.70	15.88

[a] The Chancel method is an empirical test for estimating the degree of fineness, usually employed in sulphur determinations. The procedure used is to shake a 5 g. sample in a so-called "Sulphurimeter" or "Sulphimeter" (a long, graduated glass-stoppered cylinder) with anhydrous ether and to measure the scale division reached by the suspended material after settling. Consult V. Villavecchia. "Treatise on Applied Analytical Chemistry," (Translated by T. H. Pope), P. Blakiston's Son & Co., Philadelphia, 1918, I, 112, for details.

Oshima, Fukuda and Akashi[39] investigated the ignition temperature and rates of combustion of carbon black alone and impregnated with 5 per cent solutions of various inorganic substances. They find that the ignition temperature is lowered, and report the following values: original carbon black 508°C., washed black 497°C., carbon black and potassium hydroxide 278°C., carbon black and potassium carbonate, 286°C., and carbon black and potassium chloride 403°C. The combustion velocity was practically unaffected by the presence of the added inorganic materials.

X-ray diffraction patterns of carbon black, made with strictly monochromatic radiation, show clearly the existence of single graphite layers and indicate a heterogeneous mixture of these with graphite crystals several layers thick. (See Fig. 82.) According to Warren[40] carbon black comprises a continuous series of particles extending from the mesomorphic to the crystalline state.

It is generally considered that the property of blackness is intimately connected with particle size and that increasing color intensity runs parallel with decreasing particle diameter. The evidence for this belief, though more or less indirect and circumstantial, is considered by Wiegand and Snyder[41] to be quite convincing. Thus, from measurements of heats of wetting, Hock[42] found a correlation between increasing specific surface and increasing tinctorial power, as measured in 1 per cent mixtures of the black with lithopone. Moreover, Goodwin and Park[43] carried out experiments on the reinforcement of rubber by means of a high color black (Super Spectra) and concluded that the effect of this black indicated a smaller particle size than that of a standard rubber black. A similar conclusion has been reached from estimations of particle size by indirect methods. It is interesting to note also that color intensity is also intimately related to *oil absorption*, as can be seen from Table 54 in which the oil absorption figures refer to the amounts of pale grinding linseed oil required for a given weight of black to produce a product of fixed viscosity, while the colors were observed by the nigrometer.[44]

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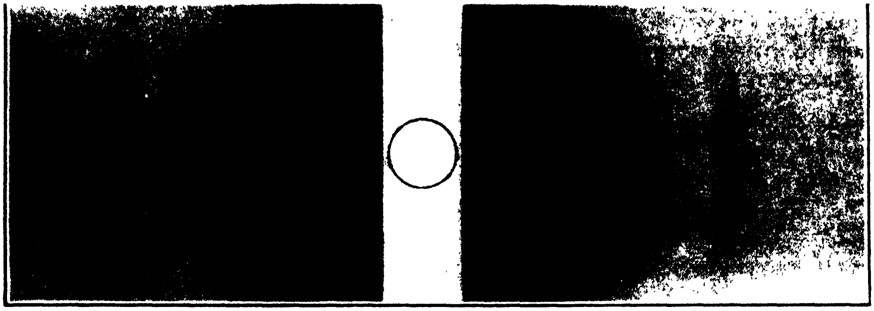
[38] M. Waldner, *Petroleum Z.*, 1936, **32**, 7.

[39] Y. Oshima, Y. Fukuda and M. Akashi, *J. Soc. Chem. Ind. Japan*, 1934, **37**, Suppl. bind. 184; *Brit. Chem. Abs.* B, 1934, 706; *Chem. Abs.*, 1934, **28**, 5205. J. E. Day and R. F. Robey (*Ind. Eng. Chem.*, 1936, **28**, 564; *Brit. Chem. Abs.* B, 1936, 675; *Chem. Abs.*, 1936, **30**, 4079) have also studied the catalytic oxidation of amorphous blacks.

[40] B. E. Warren, *J. Chem. Physics*, 1934, **2**, 551; *Chem. Abs.*, 1935, **29**, 1709.

[41] W. B. Wiegand and J. W. Snyder, *Ind. Eng. Chem.*, 1934, **26**, 413; *J. Inst. Pet. Tech.*, 1934, **20**, 362A; *Brit. Chem. Abs.* B, 1934, 485; *Chem. Abs.*, 1934, **28**, 3531.

[42] L. Hock, *Kautschuk*, 1928, **4**, 266; *Chem. Abs.*, 1929, **23**, 1772; *Brit. Chem. Abs.*, B, 1929, 180.



Courtesy B. E. Warren

Fig. 82.—X-Ray Diffraction Pattern of Carbon Black. Taken with copper *Kα* radiation.

Table 54.—*Oil Absorption of Carbon Blacks.*

Blacks	Color Intensity	Oil Absorption, Gal./100 lb.
High color	38.3	275
Medium color	29.8	196
Low color	26.9	158
Low rubber	23.8	127
Rubber color	18.3	100

In view of the importance of particle size on color intensity, it is only to be expected that the production of high-intensity blacks necessitates a more refined technic and a more careful control of operating conditions than is needed for blacks of inferior color. The conditions necessary for the manufacture of the best color blacks include a higher ratio of secondary air to hydrocarbon gas, more burning tips and closer channel settings. As a result, the yield of high color black from a given volume of gas is reduced to only five per cent of that normally obtained in the production of ordinary blacks.

The intensity of color is greatly influenced by vibration, compression and mechanical action of various kinds so that compaction of carbon blacks by agitation in the collecting bin or by compression at a later stage, must be avoided as much as possible.[45] Moreover, special care should be exercised in packing to minimize vibration in transit. Wetting down of high-intensity color blacks followed by drying to eliminate entrained air is also harmful. Wiegand and Snyder suggest this may be due to the removal of a cushion of entrained air which served to inhibit the natural adhesion or flocculation of the particle.[46]

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[43] N. Goodwin and C. R. Park, *Ind. Eng. Chem.*, 1928, **20**, 621; *Brit. Chem. Abs.* **B**, 1928, 579; *Chem. Abs.*, 1928, **22**, 3802.

[44] W. B. Wiegand and J. W. Snyder, *loc. cit.*

[45] J. W. Snyder, *Official Digest Fed. Paint and Varnish Production Clubs*, **1933** (130), 285; *Chem. Abs.*, 1934, **28**, 915.

The rise in oil absorption values of carbon blacks of increasing color intensity has proved a troublesome factor in their industrial applications since it results in greater difficulties in grinding and, subsequently, a marked tendency towards reagglomeration, seeding or flocculation. As a result of this difficulty, it has been impossible formerly to take full advantage of the improved color developments. An intensive study directed towards the improvement of surface conditions such as to provide lower interfacial tension between the black and the common dispersion vehicles, has led to the development of special blacks, such as Neo-Spectra. These, while registering a marked increase in color intensity when incorporated in linseed oil vehicles, show at the same time oil absorption values and ease of dispersion comparable with those of blacks much lower in the color scale. In a similar way it has been found possible to modify the surface characteristics of blacks so as to render them more useful in nitrocellulose lacquer media because of the possibility of employing higher concentrations of black with the resulting improvement in color and gloss.

The dispersion of lampblacks has been studied by Krauze, Pamfilov and Rosljakova[47] who found that this property varied with the medium taken and was in no case equivalent to dispersion to primary particles. The dispersing effect of different media was shown to vary with different preparations of lampblack.

MODIFICATION OF PHYSICAL CONDITION OF CARBON BLACK

Because of its extremely fine state of subdivision, the handling of carbon black in bulk presents serious difficulties, especially as regards dust formation. For this reason considerable attention has been directed towards the preparation of the so-called dustless blacks, which are essentially granules of carbon black so compounded that the individual particles adhere to one another with sufficient tenacity to render the granule mechanically stable.[48] This object is achieved by Billings and Offutt[49] by subjecting flocculent carbon black to turbulent agitation in the dry state in a drum equipped with a bladed stirring device and a more slowly moving scraper to prevent accumulation of carbon on the walls of the drum. By means of this treatment the black is agglomerated into relatively tenacious spherical granules having smooth, non-adherent surfaces, with an apparent density of more than 18 lb. per cu. ft. Burger[50] achieves similar results by passing the black between rollers. The thin plates which result are similar in appearance to fish scales and can be very conveniently employed in rubber compounding.

Another procedure[51] consists in introducing droplets of a suspension of carbon black in a liquid medium into an atmosphere in which the droplets are partially dried while they remain suspended. Thus, carbon black is dispersed in water, which may contain both protective and surface tension depression agents, and the suspension is allowed to impinge onto the surface of a rapidly rotating horizontal disc mounted near the top of a tall cylindrical drying chamber through which passes a counter-current of air. In a modification of this method, carbon black, mixed to a stiff paste with a volatile liquid such as ethyl alcohol or benzene, is fed to a rotary apparatus in which it is broken into fragments, the latter being then rapidly dried by exposure to gases at temperatures of the order of 200-260°C.[52]

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[46] It should be noted that in the Lewis process, which furnishes a low intensity black (blue undertone), the wetting process serves two important purposes, freeing of occluded matter and reducing the volume-mass ratio.

[47] K. E. Krauze, A. V. Pamfilov and E. N. Rosljakova, *J. Gen. Chem., U.S.S.R.*, 1935, **5**, 438; *Brit. Chem. Abs.* **B**, 1935, 791; *Chem. Abs.*, 1935, **29**, 5327.

[48] The products obtained by these treatments are not of high intensity blackness, according to J. W. Snyder *(loc. cit.)*. In many cases, for instance, as a filler for rubber, the degree of color is of minor importance, the principal requirement being the mechanical stability of the material.

[49] E. Billings and H. H. Offutt, U. S. P. 1,957,314, May 1, 1934, to G. L. Cabot Inc.; *Brit. Chem. Abs.* **B**, 1935, 294; *Chem. Abs.*, 1934, **28**, 4190. U. S. Reissue 19,750, Nov. 12, 1935; *Chem. Abs.*, 1936, **30**, 584. British P. 404,452, 1932; *Brit. Chem. Abs.* **B**, 1934, 354; *Chem. Abs.*, 1934, **28**, 3849.

[50] P. Burger, British P. 438,883, 1934; *Brit. Chem. Abs.* **B**, 1936, 179; *Chem. Abs.*, 1936, **30**, 3181. See also C. H. Champion, British P. 453,792, 1936; *Chem. Abs.*, 1937, **31**, 1171; *Brit. Chem. Abs.* **B**, 1936, 1079.

[51] British P. 429,088, 1935, to United Carbon Co.; *Chem. Abs.* 1935, **29**, 7030; *Brit. Chem. Abs.*, **B**, 1935, 711.

By moistening carbon black with about 40 per cent of water, sufficient to form a pasty, friable mass and from which the water is evaporated by spraying into a heated atmosphere at about 400-500°F., Grote[53] produces small round particles of carbon black with reduced dusting and soiling properties. These particles have an apparent density greater than that of the loose carbon black, and they crush easily when mixed with such materials as rubber or wax. Another method of agglomeration is to moisten the black with a volatile liquid (alcohol, water, gasoline or acetone) and mold the pasty mass into thin sheets. The latter are subdivided into small fragments and dried.[54]

The preparation of dustless carbon black has been discussed by Platonova,[55] who recommended briquetting an emulsion of 200 grams black, 24 grams sapropelite tar and 50 cc. water and drying the granules at 105°C. for three hours. Similar results were achieved by briquetting a mixture of 200 grams carbon black and 100 cc. of a 5 per cent aqueous solution of dextrin and drying for 4 hours. Both of these products gave satisfactory dispersion tests in 2 per cent aqueous ammonia.

Stable dispersions of carbon black in water are obtained by Tucker[56] in the presence of 2-6 per cent (based on the carbon black) of a soluble salt of a compound obtained by condensing a sulphonated aromatic hydrocarbon with formaldehyde. Another agent of this type is obtained by reacting 1 mole of formaldehyde with about 2 moles of β-naphthalene-sulphonic acid. The dispersing properties are improved by the addition of 1 to 10 per cent of an alkaline earth naphthenate. This is effected by dispersing the carbon black in an aqueous solution of an alkaline naphthenate, adding an alkaline-earth salt, washing and drying.[57]

According to Wiegand[58] channel blacks are improved both in blackness and workability by allowing the black to remain in free contact with the atmosphere of the burner house at 300 to 1000°C. This treatment causes partial oxidation and is said to furnish a material with a color index greater than 25 and a ratio of color index to oil-absorption index in excess of unity.[59] Damon,[60] however, prefers to heat carbon black in a rotating drum at not more than 540°C. in a current of gas containing oxygen. This treatment is said to increase the oxygen content of the black and thereby improve its color. An improved form of black is said to result

[52] British P. 437,647, 1934, to United Carbon Co.; *Brit. Chem. Abs.* B, 1936, 135; *Chem. Abs.*, 1936, 30, 2717.

[53] H. W. Grote, Canadian P. 353,730, 1935; *Chem. Abs.*, 1936, 30, 2335. See also H. J. Glaxner, U. S. P. 2,065,371, Dec. 22, 1936, to Columbian Carbon Co.; *Chem. Abs.*, 1937, 31, 1172.

[54] H. W. Grote, U. S. P. 2,040,770, May 12, 1936, to United Carbon Co.; *Chem. Abs.*, 1936, 30, 4636.

[55] A. Platonova, *J. Rubber Ind., U.S.S.R.*, 1935, 12, 161; *Chem. Abs.*, 1935, 29, 6372.

[56] G. R. Tucker, U. S. P. 2,046,757 and 2,046,758, July 7, 1936, to Dewey and Almy Chemical Co.; *Chem. Abs.*, 1936, 30, 5740. Brit. P. 414,932, 1933; *J. Inst. Pet. Tech.*, 1934, 20, 524A; *Chem. Abs.*, 1935, 29, 564; *Brit. Chem. Abs.* B, 1934, 950. French P. 764,067, 1934; *Chem. Abs.*, 1934, 28, 5612. C. W. Tucker, Canadian P. 354,103; 1935; *Chem. Abs.*, 1936, 30, 1469. Also see G. R. Tucker, Canadian P. 347,865, 1935 to Dewey and Almy Chemical Co. of Canada, Ltd.; *Chem. Abs.*, 1935, 29, 3075. See also Chapter 46.

[57] British P. 443,470, 1935, to Krebs Pigment and Color Corp.; *Brit. Chem. Abs.* B, 1936, 485; *J. Inst. Pet. Tech.*, 1936, 22, 222A; *Chem. Abs.*, 1936, 30, 5376. See also Chapter 48.

[58] W. B. Wiegand, U. S. P. 2,013,774, Sept. 10, 1935; *Chem. Abs.*, 1935, 29, 7029. British P. 450,450, 1936; *Chem. Abs.*, 1937, 31, 228; *Brit. Chem. Abs.* B, 1936, 916; *J. Inst. Pet. Tech.*, 1936, 22, 464A.

[59] W. B. Wiegand, U. S. P. 2,013,775, Sept. 10, 1935; *Chem. Abs.*, 1935, 29, 7029.

[60] E. H. Damon, U. S. P. 2,005,022, June 18, 1935, to Cabot Carbon Co.; *Chem. Abs.*, 1935, 29, 5231; *Brit. Chem. Abs.* B, 1936, 679.

also by subjecting the material to the action of hydrogen at 350-500°C. and 5 to 500 atmospheres pressure for $\frac{1}{4}$ to 10 hours.[61] To improve the oil-adsorption power of carbon black without diminishing its color intensity, Grote[62] recommends attrition in an atmosphere of carbon dioxide at 200-425°C. for 5 to 15 hours.

Another method of improving the quality of thermal blacks has been described by Frenkel.[63] Treatment is effected by injecting a mixture of the material with water into a heated gaseous medium, such as carbon dioxide or nitrogen, under a pressure and at a temperature such that steam is instantaneously generated and the carbon black is disintegrated into very fine particles of a size less than 1.0 micron. Eagles[64] proposes to inhibit the agglomeration of the fine particles of black suspended in the gaseous products of combustion by passing the gas and suspended material through a screen into a relatively cool stream of inert gas.

INDUSTRIAL APPLICATIONS OF CARBON BLACK

The characteristic physical properties of carbon black, which render it of such great technical value, are intimately associated with its extremely minute particle size, the latter being well below the resolving power of the best microscopes. Indirect measurements indicate a value of 0.025 micron for the diameter of particles of high-intensity color blacks,[65] while the particle diameter of standard rubber carbon blacks is about 0.06 micron by the ultramicroscopic count procedure.[66] In this connection it has been stated that the average particle size of the rubber black "Micronex" is of the order of 0.15 micron.[67] Irrespective of the absolute value of the diameter, there is good evidence to believe that the wide variation in physical properties (such as color, tinting power, adsorptive power) displayed by various types of black are mainly dependent on differences in particle size. Such variations in physical characteristics have an important bearing on the possible industrial applications of individual blacks.

Use of Carbon Black in Rubber Manufacture. The most important application of carbon black is in the compounding of rubber whereby the latter's tensile strength is doubled and its resistance to abrasion quadrupled.[68] In 1935, 182 million lbs. of carbon were consumed by the rubber industry in the U.S.A., about 3.3-11.9 lbs. being used in the production of a single tire depending on its size and design.[69]

Another important characteristic of blacks is their adsorptive power, which is usually measured with such substances as diphenylguanidine, methylene blue or iodine. Blacks with high adsorptive power, such as channel blacks, have the property of retarding the curing rate of rubber stocks probably by adsorptive removal of the organic accelerator. On the other hand, materials of low adsorptive power, such as the thermal blacks, do not effect retardation of cure. The question of the adsorptive power has been discussed by Wiegand and Snyder[70] who have concluded that the diphenylguanidine adsorption test correlates well with the rubber-curing behavior of broad classes of carbon black in organically accelerated mixes but the correlation is less satisfactory in the case of Micronex, a standard rubber black.

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[61] British P. 451,052. 1936, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech.*, 1936, **22**, 515A; *Chem. Abs.*, 1937, **31**, 513. French P. 796.519. 1936: *Chem. Abs.*, 1936. **30**, 6148.

[62] W. H. Grote, U. S. P. 2,066,274, Dec. 29, 1936, to United Carbon Co.; *Chem. Abs.*, 1937, **31**, 1171.

[63] G. A. Frenkel, U. S. P. 1,990.228, Feb. 5, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 1948; *Brit. Chem. Abs.* B, 1936, 85.

[64] R. H. Eagles, U. S. P. 2 015,360, Sept. 24, 1935, to J. M. Huber Corp.; *Chem. Abs.*, 1935, **29**, 7598; *Brit. Chem. Abs.* B, 1936, 679.

[65] F. E. Bartell and C. N. Smith, *Ind. Eng. Chem.*, 1929, **21**, 1102; *Brit. Chem. Abs.* B, 1930, 43; *Chem. Abs.*, 1930, **24**, 2657.

[66] S. D. Gehman and T. C. Morris, *Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 157; *Brit. Chem. Abs.* B, 1932, 613; *Chem. Abs.*, 1932, **26**, [illegible]

[67] A. Speedy, *Chemistry and Industry*, 1934, **53**, 429.

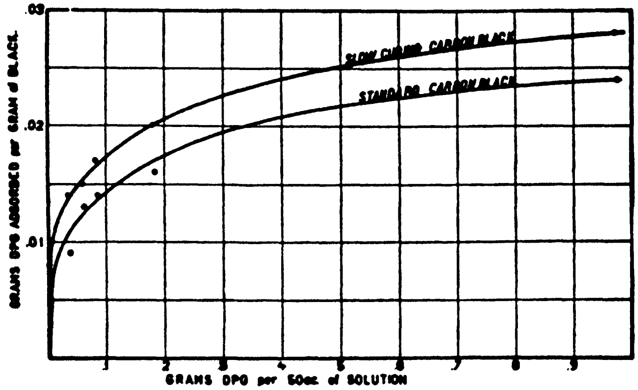
[68] For a discussion of the importance of carbon black in the rubber industry, see T. L. Garner, *Ind. Chemist*, 1935, **11**, 487; *Brit. Chem. Abs.* B, 1936, 111; *Chem. Abs.*, 1936, **30**, 2039.

[69] I. Drogin, *Chem. Met. Eng.*, 1936, **43**, 95; *Chem. Abs.*, 1936, **30**, 3174.

[70] W. B. Wiegand and J. W. Snyder, *Ind. Eng. Chem.*, 1931, **23**, 646; *Brit. Chem. Abs.* B, 1931, 705; *Chem. Abs.*, 1931, **25**, 3441.

It has been stated that rubbers having the highest stiffening, tensile properties and resistance to tear and abrasion are obtained by the use of channel blacks whereas, the thermal black, P.33, is used when softness and pliability are desired.[71]

A special black which is suited for use in rubber compounds has been prepared by Odell.[72] He treats a finely divided black produced by the thermal decomposition of hydrocarbon gas or carbon monoxide with the vapors of a rubber compounding catalyst, such as zinc or zinc oxide at about 700°C. In this manner, particles of very minute size, each consisting of a nucleus of pure carbon surrounded by a thin film of adsorbed catalyst, are obtained.



Courtesy Industrial and Engineering Chemistry
Courtesy Columbian Carbon Co.

FIG. 83.—Diphenylguanidine Adsorption Isotherms of Carbon Blacks. (W. B. Wiegand and J. W. Snyder)

Carbon Black in Manufacture of Printing Inks. The second ranking industrial application of carbon black is in the manufacture of printing inks, compounded of varnish, oils and carbon black.[73] The latter is well known as a pigment capable of providing sufficient opacity in concentrations small enough to preserve the free flowing properties of the vehicle. The consumption of carbon black in the printing ink industry in 1935 amounted to about 17 million lbs., 1 lb. of black being sufficient to print about 4,000 pages of news print. The intensity and strength of the black color displayed by carbon black were mainly responsible for its introduction and rapid development in the printing ink industry, with the result that the older type of carbon pigment, lampblack, has now almost been entirely displaced, although in a few instances mixtures of the two may be employed. However, when a variety of blacks are inspected, that showing a blue-black tone is almost invariably the one selected as constituting a strong full black. Since carbon by itself has more of a brownish tint, the addition of a toning agent, usually a blue type dye is necessary. The latter is especially practiced in the better grade inks in order to overcome a brownish tint apparent in a straight carbon black composition. In this connection it is necessary to differentiate clearly between the color of the black, by which is meant the intensity and tone of the sensation of blackness as determined visually by experienced observers, and the tinctorial strength of a black, which is a measure of its ability to impart color (blackness) to a fixed amount of a white pigment. It has been shown by Wiegand and Snyder[74] that in a series of carbons of increasing color intensity there is a maximum in tinctorial strength at a point well below the highest color values.

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[71] W. F. Russell, *The Vanderbilt News*, 1934, 4 (3), 6.

[72] W. W. Odell, U. S. P. 1,999,573, Apr. 30, 1935; *Chem. Abs.*, 1935, 29, 4212; *Brit. Chem. Abs.* B, 1936, 485.

[73] See H. J. Wolfe, "Manufacture of Printing and Lithographic Inks." MacNair-Dorland Co., New York, 1933. F. B. Wiborg, "Printing Ink," Harper and Brothers, New York and London, 1926. Also I. Drogin, *Am. Ink. Maker*, 1936, 14 (7), 17; *Chem. Abs.*, 1936, 30, 6218; *Brit. Chem. Abs.* B, 1936, 964.

Other Uses of Carbon Black. Considerable quantities of carbon black are used in the manufacture of paints and varnishes, and here again the surface properties of the black are of prime importance. The high adsorptive power associated with small particle size has been put to advantage in the improvement of insulating oils, by removing substances harmful to the electrical properties.[75] Consumption of carbon black as a coloring and reinforcing material and as a filler in such products as phonograph records and typewriter ribbons is decreasing, but, later applications in the manufacture of automobile brake bands and in the construction of dark-surfaced highways[76] and as a filler in the manufacture of carbon papers[77] are said to have commercial possibilities.

The several unique properties found especially in the thermic acetylene blacks make it possible for them not only to compete with but actually to replace cheaper blacks in certain fields.[78] In the manufacture of dry cells, thermic acetylene black is employed in connection with pyrolusite (manganese dioxide) and graphite for depolarizing purposes, due to its highly graphitic character and its extreme porosity. which enables a high absorption for the electrolyte. Because of its absorptive capacity, it is used as a filler in liquid oxygen explosives competing successfully with cheaper materials such as coal and cork fillings.

EVALUATION OF CARBON BLACKS

The applicability of a carbon black for any particular purpose can in general only be decided by a practical test carried out under conditions approaching large scale operation. Thus, those products intended for use as fillers in rubber are tested by actual rubber reinforcement tests, the resulting mix being subjected to examination for the determination of its mechanical characteristics, and resistance to abrasion and aging. Similar practical tests have been evolved in other industries, such as the printing ink industry, in which special types of black are needed.[79]

In addition to methods of examination just mentioned, there are a number of physical and chemical tests which are useful. Chemical tests include determinations of moisture, ash and extractable organic material.[80] The latter estimation is usually carried out with boiling acetone in an Underwriter's apparatus. Benzene is said to be a better extractant since it causes less penetration of the black through the fibers of the extraction thimble and is also cheaper.[81] It appears doubtful, however, whether this test has any practical significance as regards the behavior of the black in manufacturing operations.

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[74] W. B. Wiegand and J. W. Snyder. *Ind. Eng. Chem*. 1934. **26**. 413; *J. Inst. Pet. Tech.*, 1934, **20**, 362A; *Brit. Chem. Abs.* **B**, 1934, 485; *Chem. Abs.*, 1934, **28**, 3531.

[75] W. B. Wiegand, C. R. Boggs and D. W. Kitchin, *Ind. Eng. Chem.*, 1931, **23**, 273; *Brit. Chem. Abs.* **B**, 1931, 469; *Chem. Abs.*, 1931, **25**, 2277.

[76] G. R. Hopkins and H. Backus, *Min. Res. U. S. 1932-33*, 545; *J. Inst. Pet. Tech.*, 1934, **20**, 266A.

[77] M. Bandli, British P. 424.495, 1933; *Chem. Abs.*, 1935, **29**, 5657; *Brit. Chem. Abs.* **B**, 1935, 491. French P. 761.575. 1934; *Chem. Abs.*, 1934, **28** 4234

[78] C. Kaufmann, *Chem. Markets*, 1933, **33**, 217; *Can. Chem. Met.*, 1933, **17**, 93; *Chem. Abs.*, 1933, **27**, 3782.

[79] A critical review of the evaluation of carbon blacks is given by R. Klatt, W. Tietze and B. Gschaider, *Kautschuk*, 1936, **12**, 1, 25, 49; *Chem. Abs.*, 1936, **30**, 4277; *Brit. Chem. Abs.* **B**, 1936, 434.

[80] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[81] Private communication from Mr. C. C. Boardman, Thermatomic Carbon Co.

The importance of the adsorptive power of carbons, particularly in rubber manufacture, has already been discussed. For the determination of this property, diphenylguanidine in alcoholic solution is often used.[82]

Barron[83] has described a method for this determination based on the fact that if carbon black is shaken with a mixture of polar and non-polar liquids (benzene and water), it is always retained in the non-polar layer after separation. By titration of the latter the amount of iodine, phenol or benzoic acid adsorbed from the binary liquid system can now be ascertained, and by means of the distribution coefficient, the adsorption from the non-polar liquid can be calculated. The method can also be applied to the study of the effect of dispersed rubber upon the adsorptive power of carbon black for phenol and benzoic acid; the presence of 1 per cent of rubber in the benzene phase markedly reduces this.[84] It has been observed by Lemcke and Hofmann[85] that an acetylene black obtained by impingement on a cooled copper surface has an adsorptive power towards carbon tetrachloride vapor very much inferior to that of several active carbons of commercial grade.

The precautions necessary in the measurement of the color and tinctorial strength of carbon blacks have been discussed by Wiegand and Snyder.[86] They concluded that visual examination is more sensitive than the present instrumental color-testing devices and that further refinement in optical photometry is essential before the visual estimation of color differences is likely to be superseded. The importance of oil absorption values for high intensity blacks to be used as pigments in liquid vehicles has already been discussed. This property is defined by the amount of liquid vehicle required to furnish a mixture of definite viscosity when incorporated with a unit weight of carbon black under standardized conditions.[87]

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[82] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934, 249.

[83] H. Barron, *India Rubber J.*, 1934, **88**, 457; *Chem. Abs.*, 1935, **29**, 21; *Brit. Chem. Abs.* B, 1934, 1043.

[84] J. R. Baylis (*Water Works and Sewerage*, 1933, **80**, 220; *Brit. Chem. Abs.* B, 1934, 485; *Chem. Abs.*, 1934, **28**, 1429) utilized the adsorption of phenol from dilute aqueous solutions in the evaluation of activated carbon.

[85] W. Lemcke and U. Hofmann, *Z. angew. Chem.*, 1934, **47**, 37; *Brit. Chem. Abs.* A, 1934, 250; *Chem. Abs.*, 1934, **28**, 1905.

[86] W. B. Wiegand and J. W. Snyder, *Ind. Eng. Chem.*, 1934, **26**, 413; *J. Inst. Pet. Tech.*, 1934, **20**, 362; *Brit. Chem. Abs.* B, 1934, 485; *Chem. Abs.*, 1934, **28**, 3531.

[87] For a description of these tests, see W. B. Wiegand and J. W. Snyder (*loc. cit.*).

Chapter 9

Transformation of Hydrocarbons by Electrical and Other Special Forms of Energy

Two applications of electrical energy for various conversions of petroleum hydrocarbons which are outstanding are (a) voltolization and (b) the arcing treatment of hydrocarbons to make acetylene. Voltolization undoubtedly increases the viscosity index, that is to say, it flattens the viscosity-temperature curve and tends to decrease the pour point of an oil, as has been shown by Nash and his associates.

One of the routes to greater development of chemical products from petroleum and especially petroleum gases or natural gas is that via acetylene, a very reactive hydrocarbon from which, for example, acetaldehyde, acetic acid and vinyl resins can be rather readily produced.[1]

THE ELECTRIC ARC

The decomposition of hydrocarbons in the low-tension arc and also in the high-tension electric discharge (spark discharge) results in the production of hydrogen, carbon and acetylene, the latter owing its formation to its increasing thermodynamic stability with rising temperature. In addition to acetylene, considerable proportions of olefin and diolefin hydrocarbons, including ethylene and butadiene, may also be formed particularly when the time of contact with the arc is lower than that required for optimum acetylene production.

In the case of methane, Bozhko and Orshanskii[2] noted that the low-tension arc favored acetylene formation whereas carbon and hydrogen production was promoted by the high-tension arc. Maximum cracking efficiency resulted when the initial gas contained 15 to 20 per cent methane. The rate of gas flow did not influence the character of the reaction although an increase in the rate did diminish energy consumption.

Although the electrical disintegration of methane and its immediate homologues, which are abundantly available as natural gas, has been studied mainly from the viewpoint of preparing acetylene, it is interesting to note that appreciable amounts of olefin hydrocarbon gases are formed by the action of the low-tension arc on some of the heavier hydrocarbon oils. Thus, Fester, di Filippo and Patrone[3] found that the action of an iron arc on kerosene resulted in a gas containing 27.5-35.7 per cent of ethylene and 1.0-4.2 per cent acetylene, while a copper arc gave a gas having 46.7 per cent of ethylene and 7.9 per cent acetylene. When a carbon arc was used, very much more acetylene was formed, the gaseous product containing 34.0 per cent ethylene and 25.5 per cent acetylene. These investigators believed that electric arc cracking is better for the preparation of olefins for synthetic purposes than pyrolysis. Riedelsberger[3a] caused a film of liquid hydrocarbons to flow down the inside of the wall of an arc furnace in which the arc burns in a stream of hydrogen or in a gas consisting mainly of hydrogen.

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[1] For the production of acetaldehyde and acetic acid from acetylene, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934. Vinyl resins from acetylene are described by Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935. See also Chapter 28, this text.

[2] N. P. Bozhko and D. L. Orshanskii, *Khim. Tverdogo Topliva*, 1936, 7, 59; *Chem. Abs.*, 1937, 31, 1578.

[3] G. A. Fester, J. di Filippo and B. Patrone, *Rev. facultad quim. ind. agr., Univ. nacl. litoral*, 1932, 2, 130; *Chem. Abs.*, 1933, 27, 5954.

The decomposition of heavy oils in the presence of a low-tension arc has also been described by Gobert,[4] who obtained by this method a gas possessing 35-40 per cent each of acetylene and hydrogen, 5-10 per cent of ethylene and its homologues and some methane and nitrogen. For the production of 1 cubic meter of gas containing 40 per cent acetylene, about 800 g. of oil were required and the energy expenditure was 3.5 kw. hrs.

Baumann, Schilling and Stadler[5] subject waste gases from cracking or hydrogenation operations to the action of a number of low-tension electric arcs in succession with inter-stage separation of acetylene between each arc. The series of arcs is operated so that the energy supply (per unit volume of gas treated) is higher than that in the preceding one and the acetylene concentration in the gas at any stage is greater than that in the one immediately preceding. It has been proposed to use an electric arc struck between a hollow electrode and the wall of the reaction vessel as counter-electrode, the contact point of the arc on the hollow electrode being quickly moved by mechanical or magnetic means.[6] Carbon deposition apparently is lessened when the striking points of the arc are caused to move rapidly on the surfaces of both electrodes. It is reported that a gas consisting mainly of propane yielded a gaseous product containing 14-16 per cent acetylene by this method. A low tension arc of 2 mm. length may be employed and the energy density maintained at about that at which a loss of material, exceeding the normal wear and tear of the electrode substance, commences.[7] Eisenhut, Stadler and Baumann[8] recommend that an energy consumption of at least 2 kw. per sec. per cc. of arc space be employed. In this instance not only gases or vapors of paraffins and olefins serve as raw materials but also fine suspensions or mists of tars or oils in such hydrocarbons.

It is well known that considerable carbon formation takes place during the electrical disintegration of methane, or similar hydrocarbons, and is suppressed by dilution of the hydrocarbon gas with hydrogen. This dilution with hydrogen prior to electrical treatment is achieved, by Baumann,[9] by cracking of the hydrocarbon gases to convert them partly into hydrogen and liquid hydrocarbons. After separation of the latter, the residual gases are passed, with addition of fresh raw material if necessary, through an electric arc for the production of acetylene. Fischer and Peters[10] subject a mixture of methane, or other hydrocarbons and at least an equal amount of steam to the action of an electrical discharge at very low pressures, e.g., 80 mm.

[3a] W. Riedelsberger, German P. 587,129, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 717.

[4] Gobert, *J. Acetylene*, 1934, No. 92, 948; *Chimie et industrie.*, 1935, **33**, 103; *Chem. Abs.*, 1935, **29**, 2855; *Brit. Chem. Abs.* **B**, 1935, 1052. See also, S. Ya. Miloslavskii and D. L. Glizmanenko, *Avtogennoe Delo (U.S.S.R.)*, 1935, **6** (8), 29; *Chem. Abs.*, 1936, **30**, 3976.

[5] P. Baumann, H. Schilling and R. Stadler, U. S. P. 1,992,598, Feb. 26, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 2461. French P. 750,521, 1933; *Chem. Abs.*, 1934, **28**, 717. British P. 397,987, 1933; *Brit. Chem. Abs.* **B**, 1933, 951; *Chem. Abs.*, 1934, **28**, 1936.

[6] P. Baumann, H. Schilling and R. Stadler, German P. 598,140, 1934, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech.*, 1934, **20**, 581A; *Chem. Abs.*, 1934, **28**, 5350. British P. 389,165, 1933; *Chem. Abs.*, 1933, **27**, 4490; *Brit. Chem. Abs.* **B**, 1933, 377.

[7] P. Askenasy, C. Rossetti and J. Tausz, U. S. P. 1,951,961, Mar. 20, 1934, to Soc. pour l'ind. chim. a Bale; *Chem. Abs.*, 1934, **28**, 3315.

[8] O. Eisenhut, R. Stadler and P. Baumann, U. S. P. 1,941,077, Dec. 26, 1933; *Chem. Abs.*, 1934, **28**, 1283; British P. 370,414; 1930; *Brit. Chem. Abs.* **B**, 1932, 586; *Chem. Abs.*, 1933, **27**, 2888; German P. 611,113, 1935; *Chem. Abs.*, 1935, **29**, 3923; all to I. G. Farbenind. A.-G.

[9] P. Baumann, German P. 606,011, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1332.

[10] F. Fischer and K. Peters, German P. 591,756, 1934; *Chem. Abs.*, 1934, **28**, 2731; *J. Inst. Pet. Tech.*, 1935, **21**, 223A.

The simultaneous generation of acetylene and high grade carbon black has been disclosed by a number of workers although somewhat different procedures have been recommended. In the process of Baumann, Stadler, Schilling and Bückert[11] a gas rich in methane is first subjected to electrical arc treatment so that carbon black is formed from part of the gas. After removal of the black and unsaturated hydrocarbons formed, the resulting gaseous products are preheated and then passed through a second arc for acetylene manufacture. Eisenhut, Schilling and Baumann[12] suggest that after electrical treatment the gas and carbon black issuing from the arc space be passed, in a whirling motion, directly into a large cooled free space in such a way that the solid remains suspended in the gas and is prevented from being deposited on the heat-conducting surfaces. After the cooling operation the black is separated from the gases. . In the decomposition of mineral oils,[13] the arc is located beneath the surface and fresh material is introduced at such a rate that a 5-15 per cent suspension of carbon in oil is continually withdrawn.[14] The production of carbon blacks by electro-thermal dissociation of liquid hydrocarbons has been described also by Jakosky.[15]

Transformation of hydrocarbons under the action of a luminous arc produced by a direct-current generator has been disclosed by Baumann, Krapp, Stadler and Speidel.[16]

Gases from the electrical decomposition of hydrocarbons contain, in addition to acetylene and hydrogen, varying proportions of highly unsaturated compounds, such as diacetylene, allene, allylene and butadiene. Removal of these impurities is effected either by passage over an adsorbent such as active carbon or silica gel[17] or by cooling the gas mixture to about —70°C. to condense them.[18] According to Zobel and Reich,[19] treatment with a chloride or an acid having a polymerizing action, as, for example, aluminum chloride or sulphuric acid, is effective in the removal of unsaturated impurities. In other instances acetylene is absorbed by washing with a solvent, such as ethyl alcohol or acetone, at a temperature below —81.5°C., the triple point of acetylene.[20] After absorption, the residual gas is applicable for use in the destructive hydrogenation of distillable carbonaceous substances.[21]

Lead alkyl compounds are said by Sullivan and Diwoky[22] to be produced by the action of a high-tension electric arc of about 250,000 volts on liquid or gaseous

[11] P. Baumann, R. Stadler, H. Schilling and H. Buckert, U. S. P. 1.984.957, Dec. 18, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1021.

[12] O. Eisenhut, H. Schilling and P. Baumann, U. S. P. 2.002.003, May 21, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 4274. German P. 603,742, 1934; *Chem. Abs.*, 1935, **29**, 691; *J. Inst. Pet. Tech.*, 1935, **21**, 101A.

[13] For a discussion of the properties of resinous insulating oils under the influence of electric discharge, see G. W. Nederbragt, *J. Inst. Elec. Engrs.*, 1936, **79**, 282; *J. Inst. Pet. Tech.*, 1936, **22**, 509A.

[14] British P. 419,884, 1933, to Electroblacks Inc.; *Brit. Chem. Abs.* **B**, 1935, 180.

[15] J. J. Jakosky, U. S. P. 1,941,009, Dec. 26, 1933, to Electroblacks Inc.; *Chem. Abs.*, 1934, **28**, 1483. U. S. P. 1,965,925, July 10, 1934; *Chem. Abs.*, 1934, **28**, 5350; *Brit. Chem. Abs.* **B**, 1935, 462.

[16] P. Baumann, K. Krapp, R. Stadler and W. Speidel, German P. 600.584, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 7178. K. Krapp, R. Stadler and W. Speidel, German P. 601.641, 1934; *Chem. Abs.*, 1934, **28**, 7178.

[17] O. Eisenhut and H. Schilling, German P. 594,161, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 3315.

[18] H. Bückert, R. Stadler and H. Tanneberger, German P. 615.834, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 7834. U. S. P. 1.945,592, Feb. 6, 1934; *Chem. Abs.*, 1934, **28**, 2371. See also Chapter 4 for purification of acetylene.

[19] F. Zobel and H. Reich, German P. 630,249, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 5597.

[20] P. Baumann, H. Tanneberger and H. Schilling, U. S. P. 1.942.131, Jan. 2, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1611.

[21] M. Müller-Cunradi, O. Eisenhut and H. Schilling, U. S. P. 1,959,924, May 22, 1934, to Standard-I. G. Co.; *Chem. Abs.*, 1934, **28**, 4572; *J. Inst. Pet. Tech.*, 1934, **20**, 466A.

[22] F. W. Sullivan, Jr. and F. F. Diwoky, U. S. P. 1.938.547, Dec. 5, 1933, to Standard Oil Co. of Indiana; *Chem. Abs.*, 1934, **28**, 1182; *Brit. Chem. Abs.* **B**, 1934, 918. See also, F. W. Sullivan, Jr. and V. Voorhees, U. S. P. 1.938.546 Dec. 5, 1933, to Standard Oil Co. of Indiana; *Chem. Abs.*, 1934, **28**, 1182; *Brit. Chem. Abs.* **B**, 1934, 918.

hydrocarbons in the presence of lead. Thus, the arc may be struck between lead electrodes immersed in the hydrocarbon and the lead alkyl compounds recovered in the pure state by fractional distillation, or as a solution in the hydrocarbon liquid in which they are formed. Dispersions of metals in hydrocarbon oils are prepared similarly by Arnold[23] using a high-frequency current.

Using zinc electrodes, Petřik[24] obtained a gas rich in hydrogen by the action of the electric arc or spark in water vapor. When carbon electrodes were used, water gas (50 per cent hydrogen and 50 per cent carbon monoxide) was produced. With the latter electrodes, ethyl alcohol and petroleum gave gases having the compositions shown in Table 55.

TABLE 55.—*Analyses of Gases from Electrical Arc or Spark Treatment of Ethyl Alcohol and Petroleum*

	Analysis in Per Cent			
Source	H_2	CH_4	CO	C_nH_{2n}
Ethyl alcohol	30-58	6.7-29	22-29	9-12
Petroleum	58-60	10-12	2-4	26-28

THE SILENT ELECTRIC DISCHARGE

Silent discharge[25] is the term used to designate the low current discharge which takes place between electrodes, separated by gaseous (or non-ionized liquid media), at high potentials but below those at which sparking occurs. The current is usually alternating and the discharge in gases at about atmospheric pressure varies in appearance according to the circumstances but in all cases the current passing is lower than when true sparking takes place. In the silent discharge in an ozonizer, the electrodes are both separated by a glass dielectric from the gaseous medium and the current passing is very small. When one or both electrodes are in direct contact with the gas, the so-called semi-corona and corona discharges result and the current passing may be considerably greater. When the gaseous medium is at relatively low pressure the phenomena of the gaseous discharge tube appear and in the resulting glow discharge the current density may be high owing to the increasing production of electrons at the lower pressures. According to Peters,[26] the low pressure glow discharge in gases approaches more nearly to an arc, as regards its chemical action, than to the silent discharge. Peters has also discussed the action of the different types of discharge arising from the use of various pressures of the gaseous medium and different potentials, densities and frequencies of the current employed.

The chemical action of the silent discharge is complex and depends on numerous factors including pressure, potential and frequency. Subjection of hydrocarbons to such electrical treatment results in (1) dehydrogenation (except with acetylene) the degree of which increases with the degree of saturation of the material treated, (2) rupture of C-C bonds particularly in long-chain hydrocarbons, and (3) polymerization of unsaturated hydrocarbons. In many cases all these reactions take place either simultaneously or in stages so that a complex mixture of reaction products results.

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[23] J. C. Arnold, U. S. P. 1,933,836, Nov. 7, 1933; *Brit. Chem. Abs.* B, 1934, 999; *Chem. Abs.*, 1934, 28, 630.

[24] F. Petřik, *Chem. Obzor*, 1934, 9, 43; *Brit. Chem. Abs.* B, 1935, 660; *Chem. Abs.*, 1934, 28, 5341; *Chem. Zentr.*, 1935, 1, 181.

[25] The action of the silent electric discharge on hydrocarbon gases and oils has been reviewed by A. W. Nash, J. L. Howard and F. C. Hall, *J. Inst. Pet. Tech.*, 1934, 20, 1027; *Brit. Chem. Abs.* B, 1935, 178; *Chem. Abs.*, 1935, 29, 1235; *J. Inst. Pet. Tech.*, 1935, 21, 15A.

[26] K. Peters, *Brennstoff-Chem.*, 1929, 10, 441; *Chem. Abs.*, 1930, 24, 2995; *Brit. Chem. Abs.* B, 1930, 44.

Paraffin hydrocarbons may undergo dehydrogenation or fission of the carbon chain or more complicated molecules may be formed by simultaneous polymerization and dehydrogenation.[27] According to Vanier de Saint-Aunay,[28] methane yields hydrogen, ethane, ethylene, acetylene and a small quantity of unsaturated liquid hydrocarbons. The basic reaction is considered by this investigator to be dehydrogenation to active radicals which condense to ethane, the latter being further dehydrogenated to ethylene and acetylene. In the glow discharge at liquid air temperatures, methane was found by Brewer and Kueck[29] to undergo almost complete conversion into ethylene and hydrogen. Decomposition of methane by the glow discharge has also been investigated by Kobozev, Vasiliev and Galibraikh.[30] They report that about 1.5 per cent of methane was transformed into olefinic and acetylenic hydrocarbons in the presence of aluminum, copper, zinc, lead or iron. However, with mercury electrodes under the same conditions the conversion of methane was 5.2 per cent, which could be increased to 14 per cent by the use of intermediate mercury electrodes or by warming the latter. The effect was ascribed to activation of the mercury vapor which imparted its energy to the methane molecules.

The products obtained by the action of the silent electric discharge on ethane and the higher paraffins consist of hydrogen, and paraffins and olefins of both higher and lower molecular weights than that of the original hydrocarbon. Thus, hexane furnished gases including propane and propene as well as a considerable amount of liquid containing hexene-1, higher pâraffin hydrocarbons of 9 to 12 carbon atoms and also cyclic hydrocarbons.[31] When ethane was passed through a glow-discharge, hydrogen and a resin were formed, indicating a process of decomposition followed by polymerization.[32] The formation of higher hydrocarbons from paraffins is an important characteristic of the silent discharge and may take place either by dehydrogenation followed by polymerization of the unsaturated intermediate, or directly by simple doubling of the paraffin molecule to give an ion cluster followed by elimination of hydrogen. The latter mechanism was suggested by Lind and Glockler,[33] who obtained a mixture of octanes and octenes from butene. Whatever the mechanism of the change, liquid paraffin hydrocarbons, when subjected to the action of the silent discharge, undergo an increase in viscosity and molecular weight with simultaneous evolution of hydrogen.[34] This increase (in viscosity and molecular weight) is cumulative, the effect becoming greater with time of contact and also with the power input. The optimum frequency is reported by Tarasov[35] to be 500 cycles per second. Treatment of higher paraffins, such as dodecane, with a silent discharge at 7500 volts and a frequency of 1000 cycles for 6 hours is said to result in the formation of 23-28 per cent of higher molecular weight hydrocarbons.[36] Olefins such as octene, however, yielded up to 60 per cent of polymers.

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[27] For a review of the mechanism for discharges through oils, see F. F. Vol'kenshtein, *J. Tech. Phys.* (*U.S.S.R.*), 1934, **5**, 954; *Chem. Abs.*, 1935, **29**, 520; *Brit. Chem. Abs.* **B**, 1935, 438.

[28] R. Vanier de Saint-Aunay, *Chimie et industrie*, 1933, **29**, 1011; *Chem. Abs.*, 1933, **27**, 3911; *Brit. Chem. Abs.* **A**, 1933, 694.

[29] A. K. Brewer and P. D. Kueck, *J. Phys. Chem.*, 1931, **35**, 1293; *Chem. Abs.*, 1931, **25**, 2923; *Brit. Chem. Abs.* **A**, 1931, 919.

[30] N. I. Kobozev, S. S. Vasiliev and E. E. Galibraikh, *Compt. rend. acad. sci.*, *U.R.S.S.*, 1935, **2**, 236; *Chem Abs.*, 1935, **29**, 6152; *Brit. Chem. Abs.* **A**, 1935, 943. See also S. S. Vasiliev, N. I. Kobozev and E. N. Eremin, *J. Phys. Chem.* (*U.S.S.R.*), 1936, **7**, 619; *Chem. Abs.*, 1936, **30**, 7980; *Acta Physicochim. U.R.S.S.*, 1936, **5**, 201; *Brit. Chem. Abs.* **A**, 1936, 1473.

[31] R. Vanier de Saint-Aunay, *loc. cit.*

[32] A. Balandin and A. Lieberman, *Uchenuie Zapiski* (*Moscow State Univ.*), 1934, **2**, 209; *Chem. Abs.*, 1936, **30**, 6322; *Chem. Zentr.*, 1935, **2**, 1525.

[33] S. C. Lind and G. Glockler, *J.A.C.S.*, 1929, **51**, 3655; *Brit. Chem. Abs.* **A**, 1930, 190; *Chem. Abs.*, 1930, **24**, 333.

[34] F. Evers, *Siemens-Z.*, 1935, **15**, 125; *Chem. Abs.*, 1935, **29**, 4256. The gaseous products of the action of the silent discharge on heptane have been examined by C. C. Christen, *Anales inst. investigaciones cient. technol.*, 1930, **1**, 71; *Brit. Chem. Abs.* **A**, 1934, 39; *Chem. Abs.*, 1933, **27**, 4743. E. G. Linder (*Phys. Rev.*, 1930, **36**, 1375; *Chem. Abs.*, 1931, **25**, 3750; *Brit. Chem. Abs.* **A**, 1931, 179) has studied the rate of gas evolution from the vapors of hydrocarbons from *n*-pentane to tetradecane in the silent discharge.

[35] G. Ya. Tarasov, *Compt. rend. acad. sci.*, *U.R.S.S.*, 1934, **4**, 398; *Chem. Abs.*, 1935, **29**, 3145; *Brit Chem. Abs.* **B**, 1935, 293; *J. Inst. Pet. Tech.*, 1935, **21**, 88A.

It appears that unsaturated hydrocarbons not only undergo extensive polymerization but also dehydrogenation and redistribution of hydrogen atoms. Under conditions favoring the formation of primary products, namely at low temperatures and with rapid withdrawal of the reaction products from the discharge zone, Mignonac and Vanier de Saint-Aunay obtained 1-butene and 1-hexene from ethylene and straight chain trimers from acetylene.[37] Later work of de Saint-Aunay[38] indicated that the three main reactions taking place in the case of ethylene were (1) polymerization to butene and hexene, (2) dehydrogenation to acetylene and hydrogen and (3) hydrogenation by the liberated hydrogen to ethane, butane and other paraffins. Balandin, Eidus and Zalogin[39] subjected ethylene to the action of a high-frequency discharge of 5-8 watts at 15,000 volts. In a closed system the products consisted of a thick oil having a molecular weight of about 500 and a gas containing hydrogen and paraffin hydrocarbons. On the other hand, butadiene and acetylene were formed in a circulatory system. The proportion of butadiene was dependent on the rate of circulation and on the proportion of hydrogen mixed with the ethylene prior to treatment. A chain mechanism was suggested by these investigators to explain the results. Polymerization of several liquid olefin hydrocar-

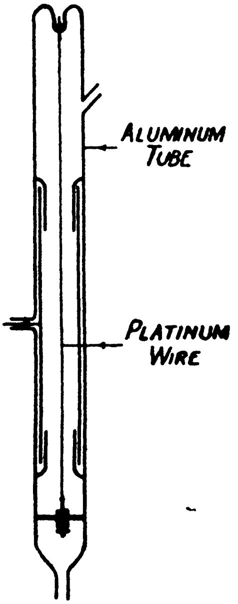

Fig. 84
Aluminum Corona Discharge Tube. (S. C. Lind and G. Glockler)

Courtesy Journal of American Chemical Society bons under the action of a high-frequency silent discharge of 7500 volts for 6 hours has been studied by Petrov and Bogoslovskaya[40] who found that low-viscosity polymers were produced in amounts up to 60 per cent.

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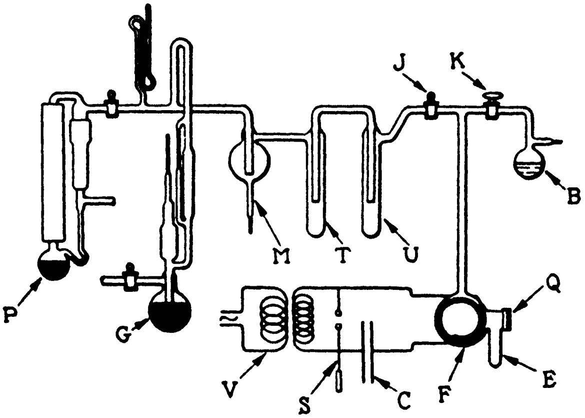
[36] A. D. Petrov and T. N. Bogoslovskaya, *Compt. rend. acad. sci. U.R.S.S.*, 1934, 4, 389; *Chem. Abs.*, 1935, 29, 3145; *Brit. Chem. Abs.* B, 1935, 292; *J. Inst. Pet. Tech.*, 1935, 21, 88A.

[37] G. Mignonac and R. Vanier de Saint-Aunay, *Compt. rend.*, 1929, 188, 959; 1929, 189, 106; *Brit. Chem. Abs.* A, 1929, 537, 1037; *Chem. Abs.*, 1929, 23, 3437, 4668.

[38] R. Vanier de Saint-Aunay, *Chimie et industrie*, 1933, 29, 1011; *Chem. Abs.*, 1933, 27, 3911; *Brit. Chem. Abs.* A, 1933, 694.

[39] A. A. Balandin, Ya. T. Eidus and N. G. Zalogin, *Gelehrte Schriften Univ. Moskau*, 1934, 2, 213; *Compt. rend. acad. sci. U.R.S.S.*, 1934, 4, 132; *Chem. Abs.*, 1935, 29, 6153; *Brit. Chem. Abs.* A, 1935, 192.

Aromatic hydrocarbons were also transformed by the silent discharge, the products including hydrogen, acetylene, polynuclear aromatic hydrocarbons and insoluble solid shellac-like bodies. The decomposition of benzene vapor at 100°C. was investigated by Vanier de Saint-Aunay.[41] He obtained a gas, containing 33 per cent acetylene and 52 per cent hydrogen, as well as a liquid mixture from which biphenyl and two isomeric dihydrobiphenyls were isolated. It was believed that polymerization to dihydrobiphenyl first occurred and this was subsequently dehydrogenated to biphenyl. In addition, depolymerization to acetylene also took place accompanied by hydrogenation of the acetylene to ethylene and ethane by hydrogen liberated in the biphenyl formation. Evidence for the production of biphenyl, biphenylene and more complex products from benzene in the electrodeless discharge was secured by Hiedemann.[42] The decomposition of benzene vapor at low pressures in the electrodeless discharge has also been examined spectroscopically by Harkins and Gans[43] who found indications of the transient existence of C^+ ions, atomic carbon and hydrogen and "CH and C_2 molecules." A brown,



Courtesy Journal of American Chemical Society

FIG. 85.—Apparatus Employed in Spectroscopic Study of Effects of Electrodeless Discharge. (W. D. Harkins and D. M. Gans)

B.	Supply bulb	M.	Trap
C.	Condenser	P.	Diffusion pump
E.	Trap	Q.	Window
F.	1-Liter pyrex flask	S.	Spark gap
G.	McLeod gage	T.	Liquid air trap
J.	Stopcock	U.	Liquid air trap
K.	Stopcock	V.	Transformer

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[40] A. D. Petrov and T. N. Bogoslovskaya, *Compt. rend. acad. sci.* (*U.R.S.S.*), 1934, **4**, 389; *Chem. Abs.*, 1935, **29**, 3145; *Brit. Chem. Abs.* **B**, 1935, 292; *J. Inst. Pet. Tech.*, 1935, **21**, 88A. Also A. D. Petrov, *Khim. Tverdogo Topliva*, 1934, **5**, 632; *Chem. Abs.*, 1935, **29**, 3503.

[41] R. Vanier de Saint-Aunay, *Chimie et industrie*, 1933, **29**, 1011; *Chem. Abs.*, 1933, **27**, 3911; *Brit. Chem. Abs.* **A**, 1933, 694.

[42] E. Hiedemann, *Ann. Physik*, 1929, (5) **2**, 221; *Chem. Abs.*, 1929, **23**, 4858; *Brit. Chem. Abs.* **A**, 1929, 978.

[43] W. D. Harkins and D. M. Gans, *J.A.C.S.*, 1930, **52**, 2578, 5165; *Brit. Chem. Abs.* **A**, 1930, 1171; 1931, 318; *Chem. Abs.*, 1930, **24**, 3440; 1931, **25**, 877. See also, W. D. Harkins, *Trans. Faraday Soc.*, 1934, **30**, 221; *Chem. Abs.*, 1934, **28**, 2272. E. J. B. Willey, *Trans. Faraday Soc.*, 1934, **30**, 230; *Chem. Abs.*, 1934, **28**, 2272.

insoluble solid of undoubtedly high molecular weight and having a composition corresponding to $(CH)_n$ was formed. The production of an insoluble solid material from this aromatic by the action of the brush discharge[44] and also by the Tesla discharge[45] has been observed.

Toluene vapor behaved in the silent electric discharge (at about 115°C.) in a manner similar to that of benzene, the products including a gas containing 58 per cent hydrogen, 10 per cent acetylene and its homologues, 8 per cent ethylene, 4 per cent ethane, 14 per cent methane, 3 per cent higher olefins and liquid products from which 1,2-diphenylethane (bibenzyl) was isolated.[46] In the Tesla discharge, toluene furnished a shellac-like substance as well as an aromatic liquid, from which Austin and Black[47] recovered 1,2-diphenylethane and 2,2′-dimethylbiphenyl. Under similar conditions, benzene and deuterium oxide (in the presence of platinum black) reacted with partial replacement of hydrogen (in the aromatic) by deuterium.[48] No change was observed in the absence of a catalyst or when ordinary water was substituted for deuterium oxide. The formation of gaseous products from toluene and several other alkyl benzenes in the corona discharge has been investigated by Linder and Davis.[49] They found that the yield of gas (under analogous conditions) increased with increasing molecular weight but diminished with increasing centralization of the molecule and with increasing proximity of the substituted groups in the benzene nucleus.

Razumov[50] reports that when a mixture of benzene, ammonia and oxygen is passed through a high-frequency high-tension electromagnetic field, there are formed aniline, diphenylamine, phenol and water. By maintaining the total gas pressure at the maximum conductivity of the medium, Kleinschmidt[51] produced a direct oxidation of benzene to phenol by air or carbon dioxide. He also polymerized benzene to biphenyl and oxidized and polymerized naphthalene. Working voltages of 1000 to 2000 volts (alternating current) were employed; and pressures less than 10 mm. of mercury were used.

INDUSTRIAL APPLICATION OF THE SILENT ELECTRIC DISCHARGE IN THE MANUFACTURE OF LUBRICATING OILS

An important industrial application of the action of the silent electric discharge on hydrocarbons is in the manufacture of synthetic lubricating oils, the so-called Electrion and Voltol oils, which are characterized by very low viscosity-temperature coefficients, stability to heat and oxidation, greater oiliness than straight mineral oils and good emulsifying properties.[52] This development originated from the observation of de Hemptinne that oils increased in viscosity under the influence of the silent discharge.[53] The apparatus employed consisted essentially of a horizontal cylindrical rotating drum with scoops around the inside periphery, the latter causing the oil contained in the drum to drip continuously over the electrodes located in the center of the apparatus.[54] The initial raw material was a 50 per cent fatty oil-mineral blend and during the electrical treatment the mineral oil content was increased until the final product contained only about 15 per cent of fatty oil.

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[44] A. P. Davis, *J. Phys. Chem.*, 1931, **35**, 3330; *Chem. Abs.*, 1932, **26**, 922; *Brit. Chem. Abs.* **A**, 1932, 130.

[45] J. B. Austin, *J.A.C.S.*, 1930, **52**, 3026; *Brit. Chem. Abs.* **A**, 1930, 1268; *Chem. Abs.*, 1930, **24**, 4225. J. B. Austin and I. A. Black, *J.A.C.S.*, 1930, **52**, 4552; *Brit. Chem. Abs.* **A**, 1931, 78; *Chem. Abs.*, 1931, **25**, 89.

[46] R. Vanier de Saint-Aunay, *loc. cit.*

[47] J. B. Austin, *loc. cit.* J. B. Austin and I. A. Black, *loc. cit.*

[48] J. Horiuchi and T. Koyano, *Bull. Chem. Soc. Japan*, 1935, **10**, 601; *Chem. Abs.*, 1936, **30**, 2434.

[49] E. G. Linder and A. P. Davis, *J. Phys. Chem.*, 1931, **35**, 3649; *Chem. Abs.*, 1932, **26**, 1191; *Brit. Chem. Abs.*, **A**, 1932, 348.

[50] V. K. Razumov, *Mem. Inst. Chem. Ukrain, Acad. Sci.*, 1935, **2**, 261; *Brit. Chem. Abs.* **A**, 1936, 1103.

[51] R. V. Kleinschmidt, U. S. P. 2,023,637, Dec. 10, 1935, to Arthur D. Little, Inc.; *Brit. Chem. Abs.* **B**, 1936, 1001; *Chem. Abs.*, 1936, **30**, 688.

[52] K. Wolf, *Petroleum Z.*, 1929, **25**, 95; *Chem. Abs.*, 1929, **23**, 4563. H. Brückner, *Chem.-Ztg.*, 1928, **52**, 637; *Chem. Abs.*, 1928, **22**, 3981.

[53] The investigations of this pioneer in conjunction with the Belgian firm of Cavel et Roeglers led ultimately to the commercial production of the Electrion oils in Ghent in 1912. The Ghent factory was taken over in 1914 by the Germans, who later erected a factory at Potschaffle where 1650 tons of lubricating oil for aeroplanes were produced in 1918. At the end of the World

Details of one method for the preparation of Voltol oils have been given by Isom.[55] In this process, owing to the slow voltolization of straight mineral oils, various vegetable and fatty oils, such as rape-seed, cotton-seed or fish oils, were first treated until they attained maximum viscosity after which 50 per cent of mineral oil was slowly added with continuous treatment until the viscosity approached 40° Engler at 100°C. The electrical treatment was carried out in a converter[56] at about 80°C. under a pressure of 60-65 cm. of mercury with no hydrogen initially present, the current used being 23 amperes at 4600 volts and 500 cycle frequency. Voltol oils were also manufactured by a method in which operations were conducted in an atmosphere of hydrogen.[57] Again, fatty oils were the starting materials, being gradually diluted with mineral oils during the electrical treatment until the final product, having a viscosity of 90° Engler at 50°C., contained 90 per cent mineral oil.[58]

The mechanism of voltolization has been the subject of a number of investigations. Nernst[59] concluded that dehydrogenation and polymerization of the unsaturated residues were the main reactions resulting from the electronic and ionic bombardment of the oil under the action of the discharge. A similar conclusion was reached by Eichwald[60] as a result of his work with oleic acid in an atmosphere of hydrogen, nitrogen or air. In this case, stearic acid was formed in a 16 per cent yield from oleic acid whether or not hydrogen was present. However, the hydrogen for the reduction, according to Eichwald, was obtained from the oleic acid molecule itself. A more general investigation has been contributed by Petrov and Bogoslovskaya,[61] who subjected straight-run and cracked kerosenes and also certain pure hydrocarbons to voltolization at 7500 volts and 1000 cycle frequency for 6 hours. The yields of polymers from typical olefin, paraffin and aromatic hydrocarbons were 60 per cent, 23-28 per cent and 15 per cent, respectively. Those from aromatics had the highest viscosity but the lowest viscosity index[62] while olefins and paraffins gave polymers of lower viscosity and higher viscosity index. The viscosity of the polymerized materials from olefins and paraffins could be in-

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War the production and selling rights of the Electrion oils were reacquired by the firm of Cavel et Roegiers while the German lubricating oils continued to be produced by the Deutsche Voltol Oel Gesellschaft under the name of Voltol Oils. A. W. Nash, J. L. Howard and F. C. Hall. *J. Inst. Pet. Tech.*, 1934, **20**, 1027; *Brit. Chem. Abs.* B, 1935, 178; *Chem. Abs.*, 1935, **29**, 1235; *J. Inst. Pet. Tech.*, 1935, 21, 15A.

[54] A. de Hemptinne, U. S. P. 852.662, May 7, 1907; *Chem. Abs.*, 1907, 1, 2188. For other suggested methods, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[55] E. C. Isom, *Oil & Gas J.*, 1925, **24** (13), 156; *Chem. Abs.*, 1926, **20**, 281.

[56] The converter was similar to that described by L. Hock, *Z. Elektrochem.*, 1923, **29**, 111; *Chem. Abs.*, 1923, 17, 2198.

[57] F. C. Otto, *Petroleum Engineer*, 1931, 2 (4), 112; *Chem. Abs.*, 1931, **25**, 4392. K. Wolf, *Petroleum Z.*, 1929, **25**, 95; *Chem. Abs.*, 1929, **23**, 4563.

[58] This method was used by the Rhenania Osrag Mineral Ölwerke A.-G. (at Dresden) employing the original de Hemptinne apparatus having a capacity of 900 cu. ft. (A. W. Nash, J. L. Howard and F. C. Hall, *loc. cit.*). For reviews of the Voltol process, see W. Roth, *Ind. Eng. Chem., News Ed.*, 1925, **3** (2), 7; Ullan, *Olii minerali, olii e grassi, colori e vernici*, 1932, **12**, 97. For a description of the Electrion process, see Decavel and Roegiers, *Chimie et industrie*, 1931, Special No., 443; *Chem. Abs.*, 1931, **25**, 3575.

[59] See K. Wolf, *Petroleum Z.*, 1929, **25**, 95; *Chem. Abs.*, 1929, **23**, 4563; *Brit. Chem. Abs.* B, 1929, 232. H. L. Kaufmann, *Refiner*, 1929, **8** (7), 122.

[60] E. Eichwald, *Z. angew. Chem.*, 1922, **35**, 505; *Chem. Abs.*, 1923, 17, 60; *J.C.S.*, 1922, **122**, 982. *Z. deut. Oel-Fett-Ind.*, 1924, **44**, 241; *Chem. Abs.*, 1925, **19**, 1061. See also Carleton Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., Inc., New York, 3rd Ed., **1930**.

[61] A. D. Petrov and T. N. Bogoslovskaya, *Compt. rend. acad. sci., U.R.S.S.*, 1934, **4**, **389**; *Chem. Abs.*, 1935, **29**, 3145; *Brit. Chem. Abs.* B, 1935, 292.

[62] For a discussion of the term *viscosity index* see Chapter 50.

creased by adding naphthene and aromatic hydrocarbons before treatment and the energy expenditure was reduced by such addition.

The effect of varying conditions on the viscosity of the product formed by subjecting cracked kerosene to the action of a silent discharge of 4 to 14 kv. in a Siemen's ozonizer was investigated by Tarasov.[63] The reaction was carried out in an atmosphere of hydrogen and under reduced pressure. Under constant electrical conditions the viscosity increased with the time of application of the discharge, this increase being more rapid after the first 6 hours. The optimum frequency was found to be 500 cycles per second and, at a constant frequency and contact time, the viscosity of the product was raised with increasing electrical power.

For the preparation of lubricating oils by voltolization a wide range of materials, including middle fractions of cracked brown coal tar,[64] hydrogenated and cracked coal tar,[65] alkylated naphthalenes[66] and halogenated paraffins, mixed with aromatics or olefins,[67] have been proposed. Products obtained by subjecting paraffin waxes having molecular weights above 330 (or substances containing substantial amounts of such waxes) to the action of the silent discharge (particularly those of high frequencies) are reported to possess lubricating properties. Addition of these bodies, after removal of hard and soft wax and middle oils, to lubricants is said to furnish oils of lower pour points and increased viscosity indices.[68] Elimination of undesirable substances from the crude products may be effected by vacuum distillation, selective solvent action,[69] fractional precipitation or adsorbent action. Electrical treatment may be carried out, for example, at temperatures of about 80°C. and under reduced pressure with a discharge of about 4000-8000 volts and 50-50,000 cycles, and for a period of time sufficient to raise the viscosity to above 12°Engler at 100°C. Voltolization is favored by the presence of foam-forming agents and also of substances promoting condensation, such as aluminum chloride, boron fluoride and zinc chloride.

Lubricants are obtained by subjecting normally liquid hydrocarbons, poor in hydrogen, to the action of silent discharges and catalytically hydrogenating the resulting products at 150-300°C. and 20-500 atmospheres.[70] Another procedure comprises subjecting an intimate mixture of oil and finely-divided substances, such as brown coal or wood charcoal, to the action of a glow discharge.[71]

The polymers secured by passage of high-tension electric discharges through 10-12 carbon-atom hydrocarbons, alcohols, esters and other organic compounds are said to reduce the pour point of viscous waxy hydrocarbon oils even if added to the extent of less than 5 per cent.[72]

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[63] G. Ya. Tarasov, *Compt. rend. acad. sci., U.R.S.S.*, 1934, 4, 398; *J. Inst. Pet. Tech.*, 1935, 21, 88A; *Chem. Abs.*, 1935, 29, 3145; *Brit. Chem. Abs.* B, 1935, 293.

[64] British P. 297,798, 1927; *Brit. Chem. Abs.* B, 1930, 180; *Chem. Abs.*, 1929, 23, 2820; British P. 303,776, 1927; *Brit. Chem. Abs.* B, 1929, 198; *Chem. Abs.*, 1929, 23, 4567; both to I. G. Farbenind. A.-G.

[65] British P. 305,553, 1927; *Brit. Chem. Abs.* B, 1929, 274; *Chem. Abs.*, 1929, 23, 4814; British P. 322,935, 1929; *Brit. Chem. Abs.* B, 1930, 134; *Chem. Abs.*, 1930, 24, 2876; both to I. G. Farbenind. A.-G.

[66] British P. 325,832, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 451; *Chem. Abs.*, 1930, 24, 4147.

[67] M. Pier and F. Christmann, German P. 556,309, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1160. French P. 702,198, 1930; *Chem. Abs.*, 1931, 25, 4117. British P. 349,071, 1930; *Brit. Chem. Abs.* B, 1931, 832; *Chem. Abs.*, 1932, 26, 2048.

[68] British P. 407,379 and 410,833, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 5220, 6298; *Brit. Chem. Abs.* B, 1934, 441, 791; *J. Inst. Pet. Tech.*, 1934, 20, 334A, 460A. French P. 749,942, 1933; *Chem. Abs.*, 1934, 28, 632. Austrian P. 141,152, 1935; *J. Inst. Pet. Tech.*, 1935, 21, 222A. M. Pier and F. Christmann, German P. 635,671, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, 31, 852. For the use of voltolized ceresin, see M. Pier and A. Eisenhut, German P. 616,833, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, 30, 606. See also G. M. Woods, *Petroleum Eng.*, 1936, 7 (13), 15; *J. Inst. Pet. Tech.*, 1936, 22, 547A.

[69] For the use of liquid propane as a selective solvent, see British P. 424,569, 1935, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1935, 346; *J. Inst. Pet. Tech.*, 1935, 21, 175A. British P. 444,244, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, 30, 6550; *J. Inst. Pet. Tech.*, 1936, 22, 268A. See also Chapter 1.

[70] British P. 433,061, 1935, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech.*, 1935, 21, 423A; *Chem. Abs.*, 1936, 30, 607; *Brit. Chem. Abs.* B, 1935, 937.

[71] M. Pier and O. Eisenhut, U. S. P. 1,964,891, July 3, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 5225.

OTHER INDUSTRIAL APPLICATIONS OF THE ACTION OF THE SILENT ELECTRIC DISCHARGE ON HYDROCARBONS

A possible application of the silent electric discharge is in the vapor-phase cracking of petroleum oils for gasoline. According to Rowland[73] the oil vapors are subjected to the action of a high-tension alternating current discharge of frequency not exceeding 10,000 cycles per second. The gasoline thus obtained is stated to need no blending and to be satisfactory as regards antiknock value. In considering the theory of the process, Rowland believes it possible for an electron moving through vapor to carry along with it a molecule of the hydrocarbon. On reaching a hot surface capable of absorbing the electron, the impact may be sufficiently great to cause disruption of the molecule.

The conversion of methane into higher hydrocarbons (e.g., propane) is effected, by Reinecke,[74] by passage of the gas under sub-atmospheric pressure through a reaction tube in which a silent electric discharge is maintained. The time of contact of the gas in the electric field is less than 0.03 second. A modification of this method comprises treating the gas (methane, ethylene, acetylene or their homologues) in a glow discharge followed by a short heating at 900°F.[75]

Several applications of the silent discharge in the purification of hydrocarbon oils have been disclosed. Thus, Bruzac[76] purifies hydrocarbons by submitting them to the action of an electric field so that impurities are electrolyzed and collect at the electrodes. A process for removal of gum-forming constituents from motor benzines has been described[77] in which the benzine is treated with a polymerizing agent, such as sulphuric acid, ferric chloride or aluminum chloride, and then subjected to the action of silent electric discharges under non-oxidizing conditions. Alternatively, treatment with the discharge may be carried out prior to polymerization.

Polymerization of resin- and gum-producing constituents of coal or manufactured gases is effected by compressing the latter to 5 atmospheres (or more) pressure, heating to 150-200°C., and then treating with a silent discharge.[78] Afterwards the gases, at the same temperature and pressure, are washed with an absorbing oil to remove the polymers. In the process of Stanton[79] for dewaxing of petroleum oils, the latter are cooled and diluted with naphtha or other solvents and the solution subjected to the action of a high-tension direct current of 125-250 kv. The oil is pumped into a hollow perforated anode from which it escapes in jets towards a horizontal cathode shell, the latter being slowly rotated. Wax is scraped continuously from the shell and oil withdrawn from the bottom.

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[72] G. H. B. Davis and J. A. Franceway, Canadian P. 346,033, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 2346.

[73] H. R. Rowland, *Oil & Gas J.*, 1930, **29** (28), 38; *Chem. Abs.*, 1931, **25**, 805. *Elec. Eng.*, 1931, **50**, 288; *Chem. Abs.*, 1931, **25**, 2373. U. S. P. 1,601,771, Oct. 5, 1926, to C. and C. Developing Co.; *Brit. Chem. Abs.* B, 1927, 67; U. S. P. 1,779,402, Oct. 21, 1930; *Chem. Abs.*, 1931, **25**, 200; *Brit. Chem. Abs.* B, 1931, 529. U. S. P. 1,837,489, Dec. 22, 1931, to Corona Conversion Corp.; *Brit. Chem. Abs.* B, 1932, 898. *Cf.* L. B. Cherry, U. S. P. 1,229,886, Jan. 12, 1917; *J.S.C.I.*, 1917, **36**, 863; U. S. P. 1,327,023, Jan. 6, 1920, and 1,345,431, July 7, 1920; *J.S.C.I.*, 1920, **39**, 260A, 716A.

[74] H. Reinecke, U. S. P. 2,028,014, Jan. 14, 1936; *Chem. Abs.*, 1936, **30**, 1394; *Brit. Chem. Abs.* B, 1937, 16.

[75] H. Tramm, German P. 615,447, 1935; *Chem. Abs.*, 1935, **29**, 6244; *J. Inst. Pet. Tech.*, 1935, **21**, 381A.

[76] J. F. A. Bruzac, French P. 752,690, 1933; *Chem. Abs.*, 1934, **28**, 979.

[77] F. Winkler and H. Häuber, German P. 592,607, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 3562. British P. 409,813, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 6297; *Brit. Chem. Abs.* B, 1934, 664. French P. 760,385, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 3562.

[78] J. R. Bircher, H. W. Seyler and J. H. Wells, U. S. P. 1,963,323, June 19, 1934; *Chem. Abs.*, 1934, **28**, 5219; *Brit. Chem. Abs.* B, 1935, 440; also Canadian P. 346,267, 1934; *Chem. Abs.*, 1935, **29**, 2339.

[79] R. E. Stanton, U. S. P. 1,940,654, Dec. 19, 1933; *Brit. Chem. Abs.* B, 1934, 919; *Chem. Abs.*, 1934, **28**, 1516.

Aldehydes are obtained by the action of a high-frequency, high-tension discharge on mixtures of paraffin hydrocarbons and oxygen, an illustration of such being the synthesis of formaldehyde from methane and oxygen.[80] If nitrogen be present also the resulting product is hexamethylenetetramine.[81] Carbon dioxide may be substituted for oxygen, though in this instance the aldehyde formed depends upon the proportion of the reactants. For example, when the concentration of carbon dioxide is equal to or greater than that of methane, formation of formaldehyde takes place.[82] When the hydrocarbon is in excess acetaldehyde is the main product.[83] In the latter instance catalysts, such as alkaline earth oxides or carbonates, may be employed.

The reduction of oxygen-containing compounds by hydrogen (or methane) in a silent discharge is described by Stuart and Try.[84] This procedure is reported applicable for preparing hydrocarbons from the creosote fraction of coal tar.

THE DECOMPOSITION OF HYDROCARBONS BY OTHER FORMS OF ENERGY

Although the photochemical decomposition of hydrocarbons as a class has received little systematic study, that of acetylene has been more carefully investigated and presents features of interest. It was shown by Reinicke[85] that although sunlight, or light from an incandescent lamp or an iron arc, did not produce any change in acetylene, this hydrocarbon (at pressures of 1 to 10 atmospheres) was polymerized to a yellow, amorphous, insoluble solid when illuminated by a quartz mercury arc. The radiation responsible for this action had a shorter wave-length than 3000 Å, since polymerization was stopped when a screen of Uviolglass was interposed between the light source and the reaction tube. By exposure of acetylene in a glass vessel at constant temperature to radiation from a "hot" mercury vapor arc, Lind and Livingston[86] obtained a brown cuprene-like product, reaction apparently taking place in one step with no side reactions or gaseous products. Light of wave lengths greater than about 2500 Å was not effective in causing polymerization and the quantum yield (i.e., ratio of molecules polymerized to light quanta absorbed) was found to be 9.2 ± 1.5. This is about half the yield per ion pair by the action of alpha particles or about equal to the average yield per ion. In this connection, Lind[87] points out that the primary step in both photochemical and ionization reactions (in the latter case such as produced by alpha particles) is probably activation involving a single electron in a single molecule. Formation of a gas ion can occur only by complete removal of an electron from the molecule which photochemical activation is attributed by Lind to a shift of an electron from its normal orbit to one of higher energy. In both ionic and photo-reactions, changes normally requiring high temperatures are induced at room temperature.

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[80] P. Nashan. U. S. P. 1.909,215, May 16, 1933, to Gutehoffungshütte Oberhausen A.-G.; *Chem. Abs.*, 1933, 27, 3675. German P. 566,516. 1933; *Chem. Abs.*, 1934, 28, 2280.

[81] P. Nashan, U. S. P. 1,930,210, Oct. 10, 1933. to Gutehoffungshütte Oberhausen A.-G.; *Chem. Abs.*, 1934, 28, 180. German P. 568,005. 1933; *Chem. Abs.*, 1934, 28, 2280.

[82] German P. 580,580, 1933, to Guttehoffungshütte Oberhausen A.-G.; *Chem. Abs.*, 1934, 28, 979.

[83] German P. 600,040, 1934, to Guttehoffungshütte Oberhausen A.-G.; *Chem. Abs.*, 1934, 28, 6376.

[84] M. Stuart and A. G. L. Try, French P. 773,818, 1934; *Chem. Abs.*, 1935, 29, 2174.

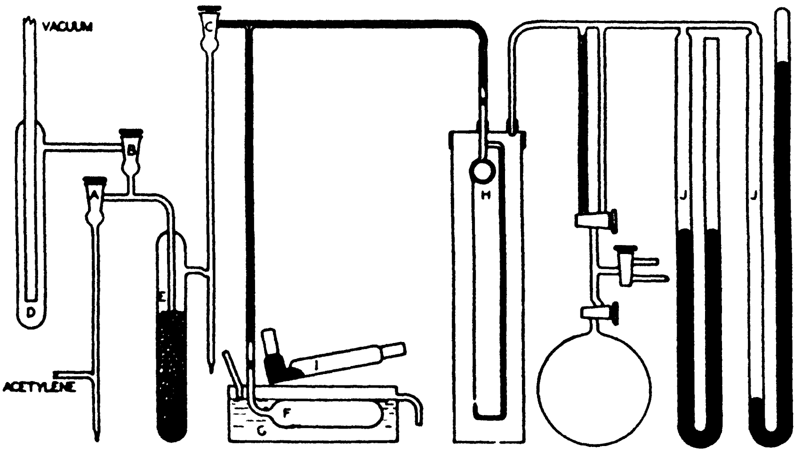
[85] H. Reinicke, *Z. angew. Chem.*, 1928, 41, 1144; *Chem. Abs.*, 1929, 23, 1352; *Brit. Chem. Abs.* A, 1928, 1340.

[86] S. C. Lind and R. Livingston, *J.A.C.S.*, 1930, 52, 4613; 1932, 54, 94; *Brit. Chem. Abs.* A, 1931, 48; 1932, 349; *Chem. Abs.*, 1931, 25, 251; 1932, 26, 1193.

[87] S. C. Lind, *J. Phys. Chem.*, 1928, 32, 573; *Brit. Chem. Abs.* A, 1928, 601; *Chem. Abs.*, 1928, 22, 4382.

In the reactions produced by ionization, clustering appears to be an important step which prevents the development of a chain reaction and also enables the molecules to withstand the shattering effect of ionizing forces. In photochemical changes, clustering around an excited molecule is also assumed by Lind to occur.

Nikoforov and Runtzo[88] observed that chemically pure bivinyl was not affected in the gaseous state by light from a quartz mercury-vapor lamp. On the other hand the technical product (70 per cent bivinyl and the remainder chiefly butene-2) after 80 hours gave a white solid, insoluble in alcohol, ether and benzene. A mercury-sensitized photochemical polymerization of cyclopropane under the influence of the 2536 Å. radiation of mercury was noted by Harris, Ashdown and Armstrong.[89] The product obtained was a viscous, colorless oil having a boiling point of nearly 300°C. at 760 mm. pressure. The structure suggested for this polymer was $(CH_2)_n$.



Courtesy Journal of American Chemical Society

FIG. 86.—Apparatus for Photochemical Polymerization of Acetylene. (S. C. Lind and R. Livingston)

A. Stopcock
B. Stopcock
C. Stopcock
D. Trap
E. Trap
F. Reaction vessel
G. Water bath
H. Manometer
I. Quartz mercury arc
J. Manometer

Polymerization of acetylene, at 0.5-10 mm. pressure and 20-500°C., by excited (electrically) mercury atoms is described by Melville.[90] The mercury atoms apparently form a complex with the hydrocarbon which then adds on more acetylene molecules. The chain length (number of acetylene molecules polymerized per excited mercury atom deactivated by the hydrocarbon) was independent of the pressure, of the rate at which the chains were started, and was not affected by packing the reaction tube. Under the same conditions ethylene polymerized, but the first stage of the reaction seemed to be dissociation into hydrogen and acetylene. Also

[88] V. K. Nikiforov and P. M. Runtzo. *Acta Physicochim. U.S.S.R.*, 1935, **3**, 335; *Chem. Abs.*, 1936, **30**, 2493; *Brit. Chem. Abs.* **A**, 1936, 1215.

[89] L. Harris, A. A. Ashdown and R. T. Armstrong. *J.A.C.S.*, 1936, **58**, 852; *Chem. Abs.*, 1936, **30**, 5126; *Brit. Chem. Abs.* **A**, 1936, 777; *J. Inst. Pet. Tech.*, 1936, **22**, 298A.

[90] H. W. Melville, *Trans. Faraday Soc.*, 1936, **32**, 258; *Chem. Abs.*, 1936, **30**, 2458.

the polymers from the latter (with ethylene as the initial material) underwent partial hydrogenation.

The catalytic influence of mercury vapor on the condensation of acetylene in ultraviolet light has been discussed by Kemula[91] and also by Toul.[92] Jungers and Taylor[93] have shown that the mercury-photosensitized polymerization of both acetylene and deuterioacetylene takes place at low pressures at a rate roughly proportional to the pressure. In the range 0.7-4 cm. the rate was found to be independent of the pressure and was 30 per cent greater with acetylene than with deuterioacetylene. It was observed by Livingston and Schiflett[94] that in addition to hard insoluble solid polymers, benzene is also formed from acetylene at 250-400°C. and 1 atmosphere pressure under the influence of light from a quartz-mercury arc. It appears, therefore, that the products of photochemical polymerization of acetylene at high temperatures closely resemble those obtained by thermal polymerization.

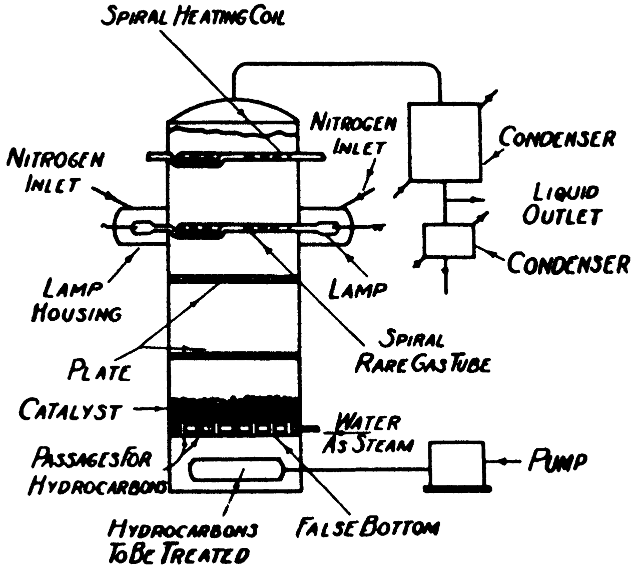


FIG. 87.—Sketch of Apparatus for Treating Hydrocarbons with Rare-Gas-Lamp Radiations. (W. O. Mitscherling)

Under the influence of radiations from a rare-gas lamp, (e.g., one containing argon), hydrocarbons, such as gasoline, are said to be oxidized to alcohols and ketones by perborates and percarbonates.[95] A metal compound, such as copper hydroxide, which increases the electrical conductivity of the hydrocarbon material

[91] W. Kemula, *Collection Czechoslov. Chem. Communications*, 1935, 7, 319; *Chem. Abs.*, 1935, **29**, 7775; *Brit. Chem. Abs.* A, 1935, 1208.

[92] F. Toul, *Collection Czechoslov. Chem. Communications*, 1935, 7, 491; *Chem. Abs.*, 1936, **30**, 1644.

[93] J. C. Jungers and H. S. Taylor, *J. Chem. Physics*, 1935, **3**, 338; *Brit. Chem. Abs.* A, 1935, 943; *Chem. Abs.*, 1935, 29, 5023.

[94] R. Livingston and C. H. Schiflett, *J. Phys. Chem.*, 1934, **38**, 377; *J. Inst. Pet. Tech.*, 1934, **20**, 300A; *Chem. Abs.*, 1934, **28**, 3663; *Brit. Chem. Abs.* A, 1934, 611.

[95] W. O. Mitscherling, U. S. P. 2,003,303, June 4, 1935, to Neon Research of Connecticut, Inc.; *Chem. Abs.*, 1935, **29**, 4771.

undergoing treatment should be present. Radiations, such as those from a positive column neon lamp, are also recommended for this purpose.[96] Fig. 87 shows an apparatus which may be employed in this case.

Under the action of α-particles and β-radiations, hydrocarbons undergo extensive decomposition and polymerization. In the case of acetylene, a solid, insoluble polymer is the main product from the action of alpha particles,[97] cathode rays[98] and high frequency electromagnetic fields.[99] During the polymerization of acetylene under the influence of alpha particles, the velocity of reaction is increased by dilution with gases such as nitrogen, helium, neon, argon, krypton, xenon and carbon dioxide. To explain this increase, it is assumed that an inert gas ion is formed capable of serving as the center of a cluster of molecules and thus promotes polymerization.[100] It is reported that methane at atmospheric pressure photochemically decomposes when irradiated with light which is transmitted through a thin fluorite window from a hydrogen discharge tube. Hydrogen and unsaturated hydrocarbons are found in the resulting products.[101]

The decomposition of hexane, cyclohexane and benzene in the positive-ray tube has been examined by Conrad[102] with the aid of the mass spectrograph. Evidence of the existence of a large number of radicals from C_1 to C_6 was obtained and the conclusion was reached that under the conditions of the discharge a free radical tends to pass into a stable compound by expulsion of a hydrogen atom with formation of a double bond. Both cyclopentane and cyclopentene under the influence of radon have been found to yield liquid products, the ratio of the hydrocarbon molecules decomposed to the number of ions being 1.7 in the case of cyclopentane and 4.5 in the case of cyclopentene.[103]

The synthesis of liquid hydrocarbons from gaseous aliphatics is described by Hillis.[104] The gases are treated with cathode rays and x-rays and the resulting material is conducted into a reaction zone between oppositely charged electrodes where it is mixed with mercury vapor (under heat and pressure) and subjected to an arc discharge in the presence of ultraviolet light. Nickel powder in the reaction zone is reported to facilitate elimination of hydrogen from the simpler molecules and formation of complex molecules with a larger number of carbon atoms.

Henry[105] prepares gasoline of high antiknock value from petroleum hydrocarbon vapors by subjecting the latter to an electromagnetic light and wave field at 24-205°C. The lower boiling fractions from the condensed gasoline are recycled through a second electromagnetic wave field to yield further quantities of liquids. As an alternative procedure, preheated vapors are led through a cracking coil (inductively heated by a high-frequency current) so that the temperature is suddenly increased and cracking takes place simultaneously.[106] The superheated gases are then expanded into a large chamber where they are exposed to the action of a high-frequency oscillating electromagnetic field.

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[96] W. O. Mitscherling, U. S. P. 2,003,898, June 4, 1935, to Neon Research of Connecticut, Inc.; *Chem. Abs.*, 1935, **29**, 4931; *Brit. Chem. Abs.* **B**, 1936, 584.

[97] S. C. Lind and D. C. Bardwell, *Science*, 1925, **62**, 422, 593; *Chem. Abs.*, 1926, **20**, 702, 1031; *Brit. Chem. Abs.* A, 1926, 654, 581; *Science*, 1936, **63**, 310; *J.A.C.S.*, 1926, **48**, 1575; *Chem. Abs.*, 1926, **20**, 2459; *Brit. Chem. Abs.* **A**, 1926, 770.

[98] J. C. McLennan, M. W. Perrin and H. J. C. Ireton, *Proc. Roy. Soc.*, 1929, **125A**, 246; *Chem. Abs.*, 1930, **24**, 23; *Brit. Chem. Abs.* **A**, 1929, 1249.

[99] R. Moens and A. Juliard, *Bull. sci. acad. roy. Belg.*, 1927, **13**, 201; *Chem. Abs.*, 1928, **22**, 31; *Brit. Chem. Abs.* **A**, 1927, 1042.

[100] S. C. Lind, D. C. Bardwell and J. H. Perry, *J.A.C.S.*, 1926, **48**, 1556. W. Mund, *J. Phys. Chem.*, 1934, **38**, 635; *Brit. Chem. Abs.* **A**, 1934, 737.

[101] P. A. Leighton and A. B. Steiner, *J.A.C.S.*, 1936, **58**, 1823; *Chem. Abs.*, 1936, **30**, 7457; *Brit. Chem. Abs.* A, 1936, 1348.

[102] R. Conrad, *Trans. Faraday Soc.*, 1934, **30**, 215; *Chem. Abs.*, 1934, **28**, 2272; *Brit. Chem. Abs.* **A**, 1933, 1270.

[103] G. B. Heisig, *J. Phys. Chem.*, 1935, **39**, 1067; *Chem. Abs.*, 1936, **30**, 384; *Brit. Chem. Abs.* **A**, 1936, 38.

[104] D. M. Hillis, U. S. P. 1,961,493, June 5, 1934; *Chem. Abs.*, 1934, **28**, 4670; *Brit. Chem. Abs.* **B**, 1935, 294.

[105] I. W. Henry, U. S. P. 1,961,358, June 5, 1934, to Ionizing Corp. of America; *Chem. Abs.*, 1934, **28**, 4896; *Brit. Chem. Abs.* **B**, 1935, 295.

In a process of Plauson,[107] liquid hydrocarbons are produced by subjecting gaseous hydrocarbons or water-gas to an intense beam of β-rays (having a velocity of at least half that of light) or to the joint effect of such β-rays and the x-rays produced from them by secondary action with such substances as quartz or feldspar. Reaction may be facilitated by the use of rotating electromagnetic fields and catalysts of the same types as those employed in the synthesis of hydrocarbons from water gas.[108] The yields of liquid hydrocarbons are reported to be increased by carrying out operations at high pressures and temperatures. If the irradiated gases contain water vapor, the products are said to include ketones and alcohols as well as liquid hydrocarbons. Liquid hydrocarbons of the paraffin and olefin series can also be made from water gas and volatile gases from coal. The treatment of the gas mixture consists in heating to not over 600°C. and subjecting to the action of ultraviolet light, an electrostatic field at about 80,000 to 100,000 volts and a nickel-tin catalyst having a trace of mercury.[109]

Discoloration of hydrocarbon motor fuels (due to exposure to light) is prevented by subjecting the liquids to actinic light and simultaneously treating with water.[110] In place of the latter an aqueous solution of methanol or glycol can be used. The proportion of water present should be about 0.01 per cent of the fuel. Alternatively, 0.05-0.5 per cent of an aliphatic monohydric acid may be added to the hydrocarbons.

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[106] I. W. Henry, U. S. P. 1,983,027, 1,983,028 and 1,983,029, Dec. 4, 1934, to Ionizing Corp. of America; *Chem. Abs.*, 1935, **29**, 589.

[107] H. Plauson, British P. 309,002, 1927; *Chem. Abs.*, 1930, **24**, 299

[108] For a discussion of this synthesis, see Chapter 52.

[109] G. F. Michot-Dupont, U. S. P. 2,033,914, Mar. 17, 1936, to Physical Chemistry Research Co.; *Chem. Abs.*, 1936, **30**, 3209.

[110] W. A. Schulze and F. E. Frey, U. S. P. 1,950,697, Mar. 13, 1934, to Phillips Petroleum Co.; *Brit. Chem. Abs.* **B**, 1935, 181.

Chapter 10

Reaction of Hydrocarbons with Steam, Carbon Dioxide and Ammonia at High Temperatures

General methods for the industrial production of hydrogen include electrolysis of water, the water-gas reaction, steam-iron reaction, pyrolysis and partial oxidation of hydrocarbons, particularly methane, and the decomposition of methane with steam.[1] Of these, the last three are of particular interest to the petroleum industry. Pyrolysis of hydrocarbons to hydrogen and carbon has been previously discussed (see Chapter 7). In this chapter the reaction of steam with, and to some extent partial oxidation of, hydrocarbons is described.

Although hydrocarbons and steam at high temperatures yield principally hydrogen and carbon monoxide (or dioxide), it is of interest to note that in some instances alcohols are formed at atmospheric pressure.[2] The formation of methyl alcohol from methane is believed to take place thus:

$$\begin{aligned} CH_4 + H_2O &\longrightarrow CO + 3H_2 \\ CO + 3H_2 &\longrightarrow CH_3OH + H_2 \end{aligned}$$

A 57 per cent yield is reported. Ethyl alcohol is said to be obtained in a similar manner from certain gas mixtures.

REACTIONS OF HYDROCARBONS WITH STEAM

In the absence of active catalysts little reaction between hydrocarbons and steam takes place except at very high temperatures. In the presence of contact agents, however, hydrogen and the oxides of carbon are produced. In the case of methane the two main reactions may be represented by:

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad (1)$$

$$\text{and} \quad CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2 \qquad (2)$$

Both of these are reversible and take place simultaneously at temperatures above 500°C. The equilibrium constants indicate that both would proceed to completion at about 1000°C.[3] Although this is true for the first reaction (in the presence of catalysts) at such temperatures, in practice the second one is suppressed (except when a very large excess of steam is present) because the carbon dioxide formed reacts with hydrogen to yield carbon monoxide and water according to the well known water-gas equilibrium:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (3)$$

In the presence of substances which catalyze the water-gas reaction, the extent to which reactions (1) and (2) proceed will be controlled by the water-gas equilibrium. At about 1000°C. this equilibrium is almost completely in favor of carbon monoxide and steam, while at temperatures of about 400°C. only a small proportion of carbon monoxide is present in the equilibrium mixture.

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[1] For a discussion of these various methods, see L. Jacque, *Ann. combustibles liquides*, 1934, **9**, 7; *J. Inst. Pet. Tech.*, 1934, **20**, 320A; *Chem. Abs.*, 1934, **28**, 3215; *Revue Ind. minerale*, 1934, **313**, 18; *Chem. Abs.*, 1934, **28**, 4859. The latter method has also been investigated by V. A. Karzhavin (*Chem. Eng. Congr. World Power Conf.*, 1936, C17).

[2] Christesco, *Chaleur & ind.*, 1934, **15** (167), 456; *Chem. Abs.*, 1934, **28**, 6423.

[3] For a discussion of these constants, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

In general, it has been found that methane and steam (at high temperatures) yield almost exclusively hydrogen and carbon monoxide. However, by using a very large excess of steam it has been possible to realize reaction (2) almost exclusively at temperatures as high as 1000°C. The latter reaction also occurs with methane and steam in the presence of catalysts at temperatures of about 500-600°C. Complete decomposition of methane apparently does not take place and high conversions are attained only with a large excess of steam over that theoretically required.

Higher saturated and unsaturated hydrocarbons may also undergo interaction with steam in the presence of catalysts, mainly hydrogen and carbon monoxide being formed at high temperatures. When operating with the homologues of methane, there appears to be a greater tendency for the formation of unstable intermediate products and fouling of the contact agent by carbonaceous deposits.

The reaction of methane with steam and carbon dioxide at temperatures of about 850°C. has been investigated by Padovani.[4] With porous refractory materials impregnated with nickel, equimolecular proportions of methane and steam were almost completely converted into carbon monoxide and hydrogen with a time of contact of about 4 seconds. The methane content of the treated gas was about .3 per cent and only traces of carbon dioxide were present. Cobalt also was satisfactory, and activators which could be incorporated included the oxides of aluminum, thorium, zinc and magnesium. It was reported that in spite of the higher temperature employed, organic sulphur did not reduce the activity of the catalysts. In view of the fact that, in the absence of steam, methane was decomposed into carbon and hydrogen in the presence of the nickel catalyst, Padovani believed that reaction between methane and steam proceeds through decomposition into carbon and hydrogen and subsequent reaction of the carbon with steam.

$$\begin{aligned} CH_4 &\longrightarrow C + 2H_2 \\ C + H_2O &\longrightarrow CO + H_2 \\ C + 2H_2O &\longrightarrow CO_2 + 2H_2 \end{aligned}$$

Fireclay impregnated with 6.4 per cent of reduced nickel was employed by Karzhavin and his collaborators[5] for the conversion of methane-steam mixtures into carbon monoxide and hydrogen at 1000°C. They observed that the activity of this catalyst was increased by the addition of as much as 1 per cent of magnesium oxide. Larger proportions of this material, however, caused a decline in activity. This nickel catalyst retained its effectiveness at 1000°C. even after prolonged use, and loss of metal as volatile nickel carbonyl was negligible. The presence of hydrogen sulphide and organic sulphur compounds (0.03-0.5 per cent) caused a slight initial reduction in catalyst activity, which then remained constant. This contrasts markedly with the rapid inactivation (by sulphur compounds) of nickel employed in the methane-steam reaction at temperatures of 500-600°C.[6] When using gaseous hydrocarbon mixtures, containing methane homologues, some deposition of soot takes place, this increasing with the proportion of hydrocarbons higher than methane in the hydrocarbon mixture. However, natural gas containing 87.4 per cent of methane has been successfully reacted with steam in a semi-commercial apparatus by Karzhavin, Elektronov and Ovchinnikov,[7] using a catalyst of nickel supported on a porous grog and at a temperature of about 1350°C. Under these conditions, a mixture of 1 volume of natural gas and 1.9 volumes of steam produced 3.3 volumes of a mixture containing 9 per cent carbon dioxide, 22 per cent carbon monoxide, 64 per cent hydrogen, 0.8 per cent methane and 4.2 per cent nitrogen. Fig. 88 shows the reaction chamber employed. In the actual operation the gas-steam mixture enters at the lower part of the apparatus, passes upward and is heated by the hot regenerative packing and catalyst. The converted gas leaves at the upper part of the chamber. When the packing has cooled so that the temperature at the top of the chamber is about 1280°C., the conversion process is interrupted. The chamber is then reheated by the combustion of natural gas with air, both entering at the top, and the combustion products leave at the bottom of the chamber. The conversion cycle is then repeated, each one lasting about 10 minutes.

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[4] C. Padovani, *Chimie et industrie*, 1934, **32**, 517; *Chem. Abs.*, 1935, **29**, 1591; *Brit. Chem. Abs.* B, 1934, 1044; *J. Inst. Pet. Tech.*, 1935, 21, 23A.

[5] V. A. Karzhavin, I. M. Boguslavskii and Z. M. Smirnova, *J. Chem. Ind.* (Moscow), 1933, **10** (8), 31; *Brit. Chem. Abs.* B, 1934, 82; *Chem. Abs.*, 1934, **28**, 1475.

[6] V. A. Karzhavin, *J. Chem. Ind.* (Moscow), 1934, **10** (2), 31; *Chem. Abs.*, 1934, **28**, 3873; *Brit. Chem. Abs.* B, 1934, 611.

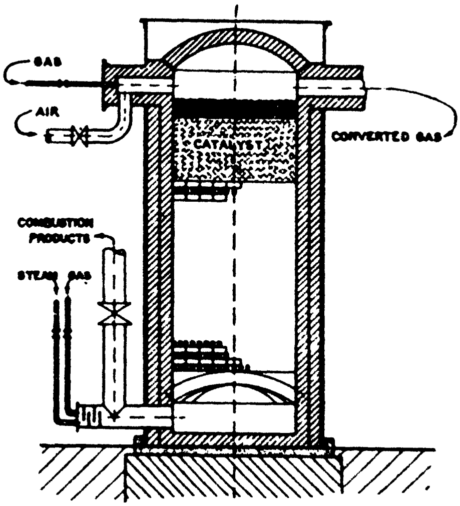

FIG. 88.
Chamber for Reaction of Natural Gas with Steam. (V. A. Karzhavin)

Courtesy Industrial and Engineering Chemistry

On the other hand, substitution of ethylene for methane results in troublesome carbon deposition.[8] Experiments with mixtures of this olefin and steam have shown that even when equilibrium is attained in an equimolecular mixture enough ethylene remains in the gas to furnish carbon by thermal decomposition. This latter reaction begins about 700°C. but can be suppressed by an excess of steam. Complete conversion of a gas containing 30 per cent of olefins and 50 per cent of methane may be obtained by preheating it to 650°C., and adding steam and 30-60 per cent of oxygen and conducting the reactants over a nickel catalyst. In this way the temperature is quickly raised to 1000-1100°C. and carbon formation is prevented.

[7] V. A. Karzhavin, N. P. Elektronov and B. M. Ovchinnikov, *Khimstroi*, 1935, 7, 459; *Chem. Abs.*, 1936, **30**, 577. V. A. Karzhavin, *Ind. Eng. Chem.*, 1936, **28**, 1042; *Chem. Abs.*, 1936, **30**, 6923; *Brit. Chem. Abs.* **B**, 1936, 1075; *J. Inst. Pet. Tech.*, 1936, **22**, 499A.

[8] V. A. Karzhavin, A. G. Leibush, B. N. Ovchinnikov and G. A. Margulis, *J. Chem. Ind.* (Moscow), 1934, No. 5, 45; *Chem. Abs.*, 1934, **28**, 5607.

According to Candea and Kühn,[9] natural gas containing 96.4 per cent of methane was almost completely transformed by reaction with 3 volumes of steam at 1000°C. in the presence of a catalyst containing iron, nickel and manganese, and with a time of contact of 20 seconds. The gaseous products contained 70 per cent of hydrogen and 20 per cent of carbon monoxide. Under similar conditions kerosene yielded 30 per cent hydrogen and 70 per cent carbon monoxide. Decomposition of a heavy residuum oil (with steam) at 800-900°C. furnished a good illuminating gas which could be employed also as a fuel for gas engines. Another use for such gases, after removal of water vapor, is in the brazing of iron or steel at 1100°C.[10]

It has been found by Schmidt[11] that coke from brown coal is effective for the conversion of methane and its homologues into carbon monoxide and hydrogen mixtures by reaction with steam at 950-1025°C. The gaseous products (containing 70 per cent of hydrogen) may be transformed into carbon dioxide and more hydrogen by further reaction with steam at 500°C. in the presence of the same agent.

From the point of view of hydrogen production from methane, the reaction

$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2$$

would appear most attractive since it yields more hydrogen than the competing reaction,

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

and also should furnish a gas mixture from which the carbon dioxide can be readily eliminated. However, for reasons already discussed, it has been found difficult to carry the former reaction to completion except in the presence of a very large excess of steam. Consequently the same overall effect has usually been attained by a two-stage process, in which high temperatures and steam are employed to decompose the hydrocarbon into hydrogen and carbon monoxide, the latter constituent being further reacted with steam at a lower temperature (in the second stage) to give carbon dioxide and hydrogen. It has been pointed out by Karzhavin[12] that complete transformation of methane (in the presence of nickel) is only possible at 500-600°C. if excess steam is employed and the carbon dioxide formed is absorbed by calcium oxide incorporated in the catalyst mass. However, regeneration of calcium carbonate at 850-900°C. destroys the activity of the catalyst. If ignited dolomite is substituted for lime, not only is carbon dioxide absorbed but any carbon monoxide present is said to be converted into carbon dioxide by the steam. According to Takenaka,[13] an active agent for accelerating the reaction,

$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2$$

at low temperatures (650°C.) consisted of a mixture of potassium carbonate, alumina and reduced nickel.

Transformation of methane, and other hydrocarbons, by steam into mixtures of hydrogen and carbon dioxide, with very little carbon monoxide, has been realized experimentally by Matignon and Seon[14] by the use of certain catalysts at temperatures above 1000°C. The best of these was zirconia while thoria ranked next and ferric oxide, alumina, ferric oxide plus 10 per cent potassium carbonate, and zirconized asbestos were less active. Passage of a gas consisting of 63.7 per cent methane, 14.4 per cent nitrogen, 10.0 per cent hydrogen, 7.3 per cent carbon monoxide, 3.8 per cent oxygen and traces of ethylene with an excess of steam over zirconia at about 1000°C. (with a time of contact of 7 seconds) furnished a product containing 74 per cent hydrogen, 17 per cent carbon dioxide and no carbon monoxide. The steam proportion was varied up to 80 times the theoretical quantity but it was found that the best results were obtained by keeping the excess small. Matignon and Seon also[14] studied the conversion of hexane, benzene, *m*-xylene, cyclohexane, cyclohexene, gas oil and fuel oil into carbon dioxide and hydrogen by reaction with steam in the presence of the zirconia catalyst at about 1000°C. At a contact time of 3 seconds, the hydrogen content of the gas from hexane was 78.5 per cent while no carbon was deposited and the carbon monoxide was very low.

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[9] C. Candea and J. Kühn. *Bull. sci. ecole polytech. Timisoara*, 1934, 5, 225; *Chem. Abs.*, 1935, 29, 8302; *Brit. Chem. Abs.* B, 1936, 532; *J. Inst. Pet. Tech.*, 1935, 21, 125A. The oxides, hydroxides or carbonates of metals of the iron group are recommended by R. Huettner and G. Wietzel, U. S. P. 2,038,566, Apr. 28, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, 30, 3953.

[10] F. P. Wilson, U. S. P. 1,988,929, Jan. 22, 1935, to General Electric Co.; *Brit. Chem. Abs.* B, 1936, 503; *Chem Abs.*, 1935, 29, 1767.

[11] R. Schmidt, *Braunkohle*, 1933, 32, 889; *Brit. Chem. Abs.* B, 1935, 292; *Chem. Abs.*, 1934, 28, 2499.

[12] V. A. Karzhavin, *J. Chem. Ind.* (Moscow), 1934, 10 (2), 31; *Chem. Abs.*, 1934, 28, 3873; *Brit. Chem. Abs.* B, 1934, 611.

[13] Y. Takenaka, *Sci. Papers, Imp. Fuel Research Inst.*, Japan, 1933, No. 15; *J. Fuel Soc., Japan*, 1933, 12, 57; *Chem. Abs.*, 1933, 27, 3585; *Brit. Chem. Abs.* B, 1933, 611.

$$C_6H_{14} + 12H_2O \longrightarrow 6CO_2 + 19H_2$$

Benzene, freed from thiophene, yielded gas containing 53 per cent of hydrogen at 1050°C. and one second contact time and a gas containing 56 per cent hydrogen at 1075°C. and 1.1 seconds contact time. At 1000°C. *m*-xylene, with twice the theoretical quantity of steam, gave a reaction product containing 64 per cent of hydrogen and those from cyclohexane and cyclohexene contained 48.5 per cent and 58.2 per cent of hydrogen, respectively. In the presence of zirconia at 1000-1050°C. reaction of steam with gas oil and mazout[15] yielded 76.2 per cent and 67.9 per cent of hydrogen, respectively. In the case of these higher hydrocarbons and steam, methane and ethylene were always observed as intermediate products but disappeared with increased contact time.

Treatment of benzene with deuterium oxide (heavy water) at 200°C., using nickel on kieselguhr as a catalyst, results in replacement of the hydrogen in the aromatic hydrocarbon by deuterium.[16] Removal of water, after each operation, and addition of fresh portions of deuterium oxide yields, successively, compounds varying in composition from C_6H_5D to C_6D_6.[17]

The equilibrium constants of the reaction,

$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2$$

at temperatures between 400-490°C. have been determined by Ghosh, Chakravarty and Bakshi,[18] using a catalyst containing nickel, thoria and ceria.

Reaction between Methane and Carbon Dioxide

In the presence of contact agents of the same type as those employed in the methane-steam reactions, methane interacts with carbon dioxide according to the reversible equation:

$$CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO - 61 \text{ kg. cal.}$$

This is essentially the sum of the two reactions,

$$CH_4 \longrightarrow C + 2H_2 \qquad \text{and} \qquad C + CO_2 \longrightarrow 2CO$$

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[14] C. Matignon and M. Seon, *Rev. petrolifere*, 1934, No. 608, 493; *Chem. Abs.*, 1935 **29**, 3119.

[15] Mazout is defined as "crude petroleum from which has been separated petroleum ether, gasoline, kerosene, and gas oil" (F. Lauer, *J. Pétrole*, 1921, **21** (6), 2; *Chem. Abs.*, 1921, **15**, 3739).

[16] P. I. Bowman, W. S. Benedict and H. S. Taylor, *J.A.C.S.*, 1935, **57**, 960; *Chem. Abs.*, 1935, **29**, 4335; *Brit. Chem. Abs.* **A**, 1935, 852.

[17] The preparation of C_6D_6 by other methods is described by H. Erlenmeyer and H. Lobeck (*Helv. Chim. Acta*, 1935, **18**, 1464; *Chem. Abs.*, 1936, **30**, 1751; *Brit. Chem. Abs.* **A** 1936 61) and N. Morita and T. Titani (*Bull. Chem. Soc. Japan*, 1935, **10**, 557; *Chem. Abs.*, 1936, **30**, 1751; *Brit. Chem. Abs.* **A**, 1936, 195). The latter investigators also prepared monodeuteriobenzene.

[18] J. C. Ghosh, K. M. Chakravarty and J. B. Bakshi, *Z. anorg. allgem. Chem.*, 1934, **217**, 277; *Brit. Chem. Abs.* **A**, 1934, 488; *Chem. Abs.*, 1934, **28**, 6613.

and it is possible that the latter effectively represent the actual mechanism of the methane-carbon dioxide reaction. The known equilibrium constant of the decomposition of methane into its elements and the carbon-carbon dioxide reaction may be combined to show the influence of temperature on the methane-carbon dioxide equilibrium. This method of calculation has been employed by Gluud, Klempt and Brodkorb,[19] whose figures for the equilibrium concentration of reactants (calculated as volume per cent of the gaseous mixture) at atmospheric pressure and at various temperatures are shown[20] in Table 56.

TABLE 56.—*Reaction* $CH_4 + CO_2 \rightleftharpoons 2H_2 + 2CO$

	Per Cent			
Temp. °C.	CH_4	CO_2	CO	H_2
450	43.5	43.5	6.5	6.5
550	28.7	28.7	21.3	21.3
650	15.5	15.5	34.5	34.5
750	3.0	3.0	47.0	47.0
850	0.8	0.8	49.2	49.2
900	0.1	0.1	49.9	49.9

It will be seen that complete decomposition of methane by carbon dioxide can only be attained at temperatures of the order of 1000°C. It has been found that catalysts for the methane-steam reaction are also effective for that between methane and carbon dioxide. Padovani and Franchetti[21] have investigated this latter reaction at temperatures of about 850°C. using porous refractory material impregnated with reduced nickel and promoters such as alumina. In a typical experiment, an equimolecular mixture of these latter two gases was passed at atmospheric pressure and a temperature of 850°C. over the catalyst impregnated with 12.5 per cent of nickel and 25.5 per cent of alumina at such a rate that the time of contact of the gases was 9.8 seconds. The gas produced contained 50.9 per cent hydrogen, 47.6 per cent carbon monoxide, 1.1 per cent carbon dioxide and 0.7 per cent methane. Nickel containing small proportions of copper was also found to be very active.

INDUSTRIAL APPLICATIONS OF THE REACTIONS OF HYDROCARBONS WITH STEAM AND CARBON DIOXIDE

The production of hydrogen from gaseous hydrocarbons is carried out industrially in a two-stage process, in which the hydrocarbons are first reacted with steam, or carbon dioxide, at high temperatures to furnish a mixture of hydrogen and carbon monoxide and the latter substance subsequently converted (in the second stage) into hydrogen and carbon dioxide by reaction with a further quantity of steam and at a lower temperature. Both stages may be effected in the presence of metallic catalysts though refractory materials of large surface and high heat content may be employed in the high temperature zone.

The chief technical difficulty confronting large scale operation is the necessity of supplying large amounts of heat to the reacting gases (owing to the high endothermicity of the reaction) at a high temperature level. In some instances this has been overcome by employing externally fired reaction chambers in conjunction with regenerative heat-exchangers of special design.[22] Wietzel and Hennicke[23] propose reaction chambers composed of highly alloyed steels, such as those containing chromium and nickel. These reactors, which are externally heated to about 600-1000°C., are constructed so that their length is very large in proportion to their cross-sectional area. For example, in one method[24] these chambers are pipes passing vertically through the roof and floor of a furnace and are arranged in rows along the sides. The burner is centered at the top and the exhaust gases are removed through openings in a horizontal flue on the bottom of the furnace. Instead of using externally heated units, the reaction between hydrocarbons and steam may be combined with some exothermic process, such as the incomplete combustion of hydrocarbons with air or oxygen. Alternatively, the operations can be carried out intermittently in the presence of heat-storing materials, which are periodically heated by direct firing. In this case the steam reaction and the firing cycle are effected in alternation exactly as in the well-known process for the manufacture of water gas.

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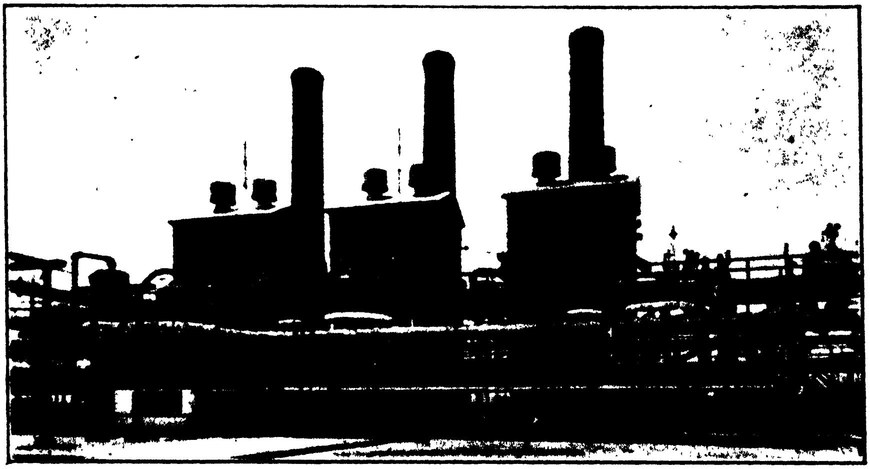
[19] W. Gluud, W. Klempt and F. Brodkorb, *Ber. Ges. Kohlentech.*, 1930, 3, 261; *Brit. Chem. Abs.* B, 1931, 325; *Chem. Abs.*, 1931, 25, 2269.

[20] The equilibrium constants of this reaction at 400-490° C. have been determined experimentally in the presence of an activated nickel catalyst by J. C. Ghosh, K. M. Chakravarty and J. B. Bakshi, *loc. cit.*

[21] C. Padovani and P. Franchetti, *Inst. Ind. Chem. Fuels,* Polytechnicum, Milan, 1932, 4, 173; *Chem. Abs.*, 1935, 29, 1229. C. Padovani, *Chimie et industrie,* 1934, 32, 517; *J. Inst. Pet. Tech.*, 1935, 21, 23A; *Chem. Abs.*, 1935, 29, 1591; *Brit. Chem. Abs.* B, 1934, 1044.



Courtesy Standard Oil Development Co.

FIG. 89.—General View of Plant for Producing Hydrogen from Hydrocarbons.

In a process described by Odell,[25] a mixture of steam and propane or butane is introduced into a highly heated fuel bed to produce a gas containing essentially hydrogen and carbon monoxide in the ratio of 2-3 to 1. It is also proposed to carry out the steam-hydrocarbon reaction by mixing the latter material with a stream of superheated steam, preheating the mixture to above 540°C. and passing it downwards, through an incandescent fuel bed (previously heated in a separate firing cycle by an air blast). The resulting product contains 2-3.5 times as much hydrogen as carbon monoxide, and is said to be free from suspended carbon resulting from the pyrolysis of the hydrocarbon material.[26]

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[22] E. Hirsch, *Bull. mem. soc. ing. civils France*, 1932, **85**, 286; *Chem. Abs.*, 1933, **27**, 2282; *Brit. Chem. Abs.* **B**, 1932, 919.

[23] G. Wietzel and W. Hennicke, U. S. P. 1,934,836, Nov. 14, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 589.

[24] W. V. Hanks, G. H. Freyermuth and G. Potts, U. S. P. 2,028,326, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 1528; *Brit. Chem. Abs.* **B**, 1936, 1207.

[25] W. W. Odell, U. S. P. 1,930,442, Oct. 10, 1934, to Columbia Engineering and Management Corp.; *Chem. Abs.*, 1934, **28**, 293; *Brit. Chem. Abs.* **B**, 1934, 746. See also, British P. 386,981, 1933; *Chem. Abs.*, 1933, **27**, 5943; *Brit. Chem. Abs.* **B**, 1933, 339.

According to Namikawa,[27] the decomposition of hydrocarbons by steam is effected over a nickel catalyst in a reaction tube placed in the center of a water-gas generator. The gaseous products then pass through hot coke surrounding the catalyst tube thus giving a mixture containing 25-34 per cent of carbon monoxide and 57-59 per cent of hydrogen. Odell[28] suggests treatment of gaseous or atomized hydrocarbons with steam in the presence of the hot coke obtained by the carbonization of solid fuels, e.g., in vertical retorts.

In another procedure, air is passed through a regenerator chamber and used to burn a combustible gas in a checker-filled, or other, reaction conduit, the waste gases serving to heat a boiler.[29] Natural gas and steam, together with carbon dioxide if higher ratios of carbon monoxide to hydrogen are desired, are then passed through the reaction chamber and regenerator in a reverse direction to the fuel gas, and the cycle of operations is repeated.

Mixtures of hydrogen and carbon monoxide were produced by Russell and Hanks[30] by reaction of methane and steam at temperatures above 760°C. in a tower packed with a catalyst. The latter consisted of alumina, or rare-earth oxide, impregnated with finely-divided nickel or cobalt. Heating was accomplished by surface combustion of gas-air mixtures on porous fireclay in a vertical tube extending the whole length of the longitudinal axis of the tower. The gases resulting from this process were then passed with more steam over a ferric oxide catalyst below 550°C. to yield carbon dioxide and hydrogen. The former was removed by appropriate scrubbers.

A combustible gas has been obtained by Odell[31] by the reaction of gaseous hydrocarbons and steam. He describes an apparatus in which the gaseous mixture is passed along refractory bricks at incandescent heat. The resulting gas, rich in hydrogen, is then admixed with a gas containing nitrogen oxides. Part of the hydrogen reduces the nitrogen oxides to nitrogen and water. This results in a nitrogen oxide-free gas, useful where a non-corrosive gas is required.

In a number of processes, part of the heat required for the endothermic reaction is supplied by admixture of oxygen (usually in the form of air) with the reactants, whereby partial combustion of the hydrocarbon (e.g., methane) is

$$CH_4 + \tfrac{1}{2}O_2 \longrightarrow CO + 2H_2 + 8 \text{ kg. cal.}$$

effected. When air is used as a source of oxygen, the resulting gas mixture will, of course, contain nitrogen. It has been shown by Padovani and Franchetti[32] that the partial combustion of methane, or gases containing methane, with air or oxygen takes place smoothly and completely in the presence of nickel catalysts at temperatures of 850-1200°C. Only small amounts of undecomposed methane remain and practically no carbon dioxide is formed. Voorhees[33] suggests the application of pressures as high as 300 atmospheres, the resulting carbon monoxide being subsequently converted into carbon dioxide and hydrogen by catalytic reaction with steam at the same pressure.

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[26] W. W. Odell, U. S. P. 1,930,443, Oct. 10, 1934, to Columbia Engineering and Management Corp.; *Chem. Abs.*, 1934, **28**, 293; *Brit. Chem. Abs.* B, 1934, 746.

[27] T. Namikawa, Japanese P. 98,957, 1933, to The Minister of Navy; *Chem. Abs.*, 1933, **27**, 5944.

[28] W. W. Odell, U. S. P. 1,968,053, July 31, 1934; *Brit. Chem. Abs.* B, 1935, 537; *Chem. Abs.*, 1934, **28**, 5970.

[29] W. D. Wilcox, U. S. P. 1,903,845, Apr. 18, 1933; *Brit. Chem. Abs.* B, 1934, 134; *Chem. Abs.*, 1933, **27**, 3321.

[30] R. P. Russell and W. V. Hanks, U. S. P. 1,951,774, Mar. 20, 1934, to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1935, 452; *Chem. Abs.*, 1934, **28**, 3563.

[31] W. W. Odell, U. S. P. 2,025,071, Dec. 24, 1935; *Chem. Abs.*, 1936, **30**, 1214; *Brit. Chem. Abs.* B, 1936, 819.

[32] C. Padovani and P. Franchetti, *Giorn. Chim. Ind. Appl.*, 1933, **15**, 429; *Chem. Abs.*, 1934, **28**, 2853.

[33] V. Voorhees, U. S. P. 1,904,908, Apr. 18, 1933, to Standard Oil Co. of Indiana; *Brit. Chem. Abs.* B, 1934, 144; *Chem. Abs.*, 1933, **27**, 3568.

Klempt[34] subjected hydrocarbons to reaction with steam in the presence of catalysts so as to be only partially converted into carbon monoxide and hydrogen. The resulting mixture was then further oxidized with air whereby the remaining hydrocarbon material was transformed chiefly into carbon monoxide and hydrogen. Carbon monoxide was changed by preferential oxidation into carbon dioxide and absorption of the latter left a mixture of hydrogen and nitrogen suitable for the ammonia synthesis.

In a process of Wilcox,[35] hydrocarbon gases together with the requisite proportions of steam and air are passed through a conduit preheated to above 1150°C. by combustion of fuel gas therein. The hot gases, consisting of a mixture of hydrogen, nitrogen and oxides of carbon, are conducted through a regenerator, and sufficient steam then added to lower their temperature to about 500°C. After this they are led successively through an iron oxide catalyst and sufficient lime to remove part of the carbon dioxide formed. More steam is added, causing their temperature to fall to about 370°C., and the gases again passed over an iron oxide catalyst and finally freed from carbon dioxide.

Wilcox[36] also prepared mixtures of hydrogen and nitrogen by reacting methane with steam at temperatures above 980°C. and mixing the resulting hot gas with preheated air so that partial combustion took place. The gases were cooled by heat exchange with ingoing materials and the carbon dioxide present then eliminated. Another procedure comprises passage of a mixture of hydrocarbon gas and steam through a conduit filled with permeable refractory material previously heated to above 1090°C. by an air-gas blast.[37] Simultaneously with the steam reaction (in which the gas direction is countercurrent to the direction of the combustion gases during the heating cycle) a controlled volume of air, preheated to above 980°C., is introduced at an intermediate point in the reaction zone. The temperature is raised by the ensuing partial combustion and by adjusting the volume of air, hydrogen-nitrogen mixtures of predetermined composition can be obtained. Wilcox[38] has also developed a process in which the requisite amount of oxygen is added to the hot products of the methane-steam reaction after the latter has proceeded only 80 per cent towards completion. The steam reaction is carried out in reactors externally heated to above 980°C. and the oxygen addition is so regulated that all the residual methane is converted into carbon monoxide and all hydrogen in excess of twice the volume of carbon monoxide is oxidized to steam. The resulting mixture can be utilized for methanol synthesis. A closed heat-recovery system for use in the interaction of methane with a large excess of steam (0.8-1.9 lb. per cu. ft. of dry gas) has been described by Svanoe.[39]

In addition to possessing high activity, the catalyst employed for the production of hydrogen and carbon monoxide from hydrocarbons and steam (or carbon dioxide) must be physically stable at high temperatures and resistant to poisoning by substances such as hydrogen sulphide.[40] A number of these have been described. For example, a paste consisting of a mixture of the hydroxides or carbonates of iron, nickel or cobalt and chromium or aluminum hydroxide is heated to remove uncombined water and then further dried at 870-1040°C. for 12 hours to 3 days.[41] During this latter period the mass is continuously treated with a current of gas free from catalyst poisons. Another procedure comprises impregnating alundum cement with nickel or cobalt nitrates, igniting the mass and then reducing the oxide with hydrogen to the metallic condition.[42] The resulting powder is mixed with black nickel oxide, the mixture pressed into cubes and the latter sintered in hydrogen at 1000°C. Woodhouse[43] recommends nickel and cerium nitrates supported on pumice and reduced in hydrogen. A catalyst was prepared by Davis and Franceway[44] by incorporating phosphoric acid with an oxide of nickel or chromium and a refractory oxide such as alumina, thoria or zirconia, and baking the mixture at a temperature below the temperature of fusion of either oxide.

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[34] W. Klempt, U. S. P. 1,931,442, Oct. 17, 1933; *Chem. Abs.*, 1934, **28**, 268.

[35] W. D. Wilcox, U. S. P. 1,962,418, June 12, 1934; *Brit. Chem. Abs.* B, 1935, 439; *Chem. Abs.*, 1934, **28**, 4844.

[36] W. D. Wilcox, U. S. P. 1,901,136, Mar. 14, 1933; *Brit. Chem. Abs.* B, 1934, 84; *Chem. Abs.*, 1933, **27**, 3063.

[37] W. D. Wilcox, U. S. P. 1,951,044, Mar. 13, 1934; *Brit. Chem. Abs.* B, 1935, 215; *Chem. Abs.*, 1934, **28**, 3535.

[38] W. D. Wilcox, U. S. P. 1,905,326, Apr. 25, 1933; *Brit. Chem. Abs.* B, 1934, 194; *Chem. Abs.*, 1933, **27**, 3567.

[39] H. Svanoe, U. S. P. 1,988,759, Jan. 22, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1935, 1073; *Chem. Abs.*, 1935, **29**, 1291.

The conversion of liquid, semi-solid and solid hydrocarbons into noncondensable gases without deposition of carbon was effected by Banc[45] by mixing them with superheated steam and passing the mixture through a contact mass maintained at 700-1000°C. According to Brassert,[46] simultaneous passage of natural gas and low-grade gases containing carbon dioxide through a highly heated zone results in cracking of the hydrocarbons to hydrogen and carbon and reaction of the latter with carbon dioxide to give carbon monoxide.

The low temperature reaction between methane and steam (usually in considerable excess) for the production of mixtures of hydrogen and carbon dioxide has attracted attention since the latter may be eliminated by relatively simple means. In practice, however, complete decomposition of the hydrocarbon in one treatment can only be achieved by the use of a very large excess of steam. Also the reaction is strongly endothermic. For these reasons it has been found convenient generally to attain the same results in a two-stage process, as previously described.

Harter[47] proposes to convert methane, or gases rich in methane, into hydrogen and carbon dioxide by reaction with steam at 550-600°C. Catalysts such as active carbon and the oxides of iron, nickel, cobalt and copper, admixed with difficultly reducible metallic oxides, may be employed. Reactivation of the catalyst is effected by subjecting it to a gas containing hydrogen and carbon monoxide (produced by partial combustion of methane) followed by a short treatment with steam, with or without air. Another contact agent is prepared by adding a solution of potassium carbonate to an aqueous solution containing the nitrates of nickel, aluminum and magnesium, mixing the precipitate with potassium nitrate and reducing the dried mixture in a current of hydrogen.[48] Passage of 1 volume of methane and 6.2 volumes of steam over this catalyst at 450-650°C. yields a gas containing carbon dioxide and hydrogen in the proportions of 1 :4.

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[40] Removal of sulphur compounds from gaseous hydrocarbons before submitting the latter to treatment with steam is described by G. Wietzel, W. Haller and W. Hennicke, German P. 578,824, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 866.

[41] W. V. Hanks and G. W. Freyermuth, U. S. P. 1,943,821. Jan. 16, 1934, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1935, 187; *Chem. Abs.*, 1934, **28**, 2136.

[42] G. H. Freyermuth, U. S. P. 1,970,695, Aug. 21, 1934, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1936, 102; *Chem. Abs.*, 1934, **28**, 6256.

[43] J. C. Woodhouse, U. S. P. 1,960,886, May 29, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 403; *Chem. Abs.*, 1934, **28**, 4547.

[44] G. H. B. Davis and J. A. Franceway, U. S. P. 1,948,338, Feb. 20, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1934, **28**, 2882; *Brit. Chem. Abs.* **B**, 1935, 10. *Cf.* French P. 771,792, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 1594.

[45] M. Banc, French P. 772,730, 1934, to "Petrosani" Societate anonima Romana pentru exploatarea minelor de carbuni; *Chem. Abs.*, 1935, **29**, 1430.

[46] H. A. Brassert, U. S. P. 1,972,259, Sept. 4, 1934, to H. A. Brassert & Co.; *Chem. Abs.*, 1934, **28**, 6554; *Brit. Chem. Abs.* **B**, 1935, 792.

[47] H. Harter, German P. 602,111, 1934; *Chem. Abs.*, 1935, **29**, 563; *J. Inst. Pet. Tech.*, 1934, **20**, 617A. U. S. P. 1,920,858, Aug. 1, 1933; *Brit. Chem. Abs.* **B**, 1934, 565; *Chem. Abs.*, 1933, **27**, 4888. See also, German P. 581,986, 583,205, 585,419 and 585,420, 1933; *Chem. Abs.*, 1934, **28**, 1150, 1151, 1482.

[48] German P. 606,841, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 3791.

According to Porter's method,[49] only small amounts of carbon monoxide occur with the carbon dioxide and hydrogen produced. One of his catalysts may be obtained by adding an aqueous nickel and aluminum salt solution to an excess of aqueous alkali (so that the solution may be basic during precipitation), supporting the resulting mixed precipitate on magnesium oxide or magnesium fluoride and drying. In this case, the aluminum acts as a promoter for the nickel catalyst. This investigator also advocates the use of chromium or molybdenum oxides, substantially free of nickel, iron or cobalt.[49a] Another contact agent which may be employed consists of palladium admixed with the oxides of two of the following metals, magnesium, beryllium, cerium, titanium, chromium, thorium or tungsten.[49b]

Woodhouse[50] decomposed methane with steam in the presence of catalysts at a temperature of 550°C., followed by further reaction with steam, and carbon dioxide-absorption at 250-450°C. A contact agent for this low-temperature operation was made by treating a nickel salt solution with a precipitant such as calcium hydroxide.[51] The precipitate was calcined, and then reduced in an atmosphere of hydrogen. Cobalt compounds may also be used. Heat for the reaction between hydrocarbons and steam is supplied, in the process of Beekley,[52] by continuously burning fuel gas in heat-exchange relation to, but out of direct contact with, the reactants. Residual heat is afterwards removed from the combustion products by heat exchange with water from which steam for the reaction is generated.

Another modification is described by Larson[53] in which, after partial conversion of the methane-steam mixture has taken place, the temperature of the reacting gases is raised by the introduction of oxygen. The resulting partial combustion produces sufficient heat to render the hydrocarbon-steam reaction practically thermally self-supporting and heat is supplied to the inlet gases by heat exchange with the hot gaseous products.

In the process of Spalding,[54] natural gas is saturated with water vapor at 83°C. and then passed over a catalyst at 390°C. to produce carbon monoxide and hydrogen. The resulting mixture is saturated with steam and conducted through a second catalyst chamber at 330-340°C. to convert the carbon monoxide and steam into carbon dioxide and hydrogen. The hot gases are compressed to 1.5-2 atmospheres and forced through a tower down which flows the effluent water from the first two operations. In this manner the water is heated to about 120°C. before being returned to the system.

The production of hydrogen from methane was effected by Williams[55] by the use of the steam reaction at temperatures of 300-500°C. and at superatmospheric pressures. A nickel catalyst containing a large proportion of an alkaline earth oxide, such as lime, was used. As soon as oxides of carbon appeared in the reaction products, the catalyst was regenerated by heating.

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[49] F. Porter, U. S. P. 2,013,066, 1935, to Atmospheric Nitrogen Corp.; *Brit. Chem. Abs.* B, 1936, 971; *Chem. Abs.*, 1935, **29**, 7029.

[49a] F. Porter, U. S. P. 2,067,729, Jan. 12, 1937, to Atmospheric Nitrogen Corp.; *Chem. Abs.* 1937, **31**, 1564.

[49b] F. J. de Rewal, U. S. P. 2,030,283, Feb. 11, 1936, to Atmospheric Nitrogen Corp.; *Chem. Abs.* 1936, **30**, 2199; *Brit. Chem. Abs.* B, 1937, 113.

[50] J. C. Woodhouse, U. S. P. 1,960,886, May 29, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 4547; *Brit. Chem. Abs.* B, 1935, 403.

[51] J. C. Woodhouse, U. S. P. 1,959,189, May 15, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 4547; *Brit. Chem. Abs.* B, 1935, 724.

[52] J. S. Beekley, U. S. P. 1,959,151, May 15, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1935, 90; *Chem. Abs.*, 1934, **28**, 4547.

[53] A. T. Larson, U. S. P. 1,960,912, May 29, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 4547; *Brit. Chem. Abs.* B, 1935, 900.

[54] W. L. Spalding, U. S. P. 1,935,675, Nov. 21, 1933, to American Cyanamid Co.; *Brit. Chem. Abs.* B, 1934, 833; *Chem. Abs.*, 1934, **28**, 884.

[55] R. Williams, U. S. P. 1,938,202, Dec. 5, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 1150; *Brit. Chem. Abs.* B, 1935, 1010.

"REFORMING" HYDROCARBONS BY PARTIAL REACTION WITH STEAM

An important application of the reaction between hydrocarbons and steam is the so-called reforming of natural and refinery gases. The products of reforming consist of unchanged hydrocarbons as well as hydrogen and oxides of carbon and their composition may be varied by controlling the extent of reaction with steam so as to produce gaseous fuels of almost any desired calorific value from 280 to 1800 B.t.u. per cu. ft. In the Davis reforming process,[56] butane and other hydrocarbon gases of high thermal value are degraded in the presence of a catalyst of metallic nickel in a cycle of operations which includes blasting, reforming and steaming periods in which the generator is heated, cracking of the rich gases and the purging of the machine. The reactor consists of an insulated refractory-lined chamber similar to a water-gas generator and is packed with 1″ x 3″ helical coils of No. 10 gauge nickel wire. Tar and condensable oils are not formed and the activity of the nickel increases with use. Catalyst losses are said to amount to only about 2 cents per 1000 cu. ft. of gas.

Another method of reforming natural or refinery gas, developed by Perry,[57] does not involve the use of catalysts. Instead, the hydrocarbon gas is passed through an incandescent fuel bed, producing a reformed gas, a stiff pitch and deposition of carbon in the fuel bed. The fuel bed is then air-blasted to provide heat to crack more gas, after which the remaining excess carbon is converted into water-gas by steaming. The mixture of reformed and water gases has a calorific value of about 460 B.t.u. per cu. ft., and may be enriched by vaporization of liquid hydrocarbons (e.g., gas oil) with heat from the air blast gases. According to Perry,[58] 1000 cu. ft. of refinery gas of 1600 B.t.u. yields 2000 cu. ft. of 560 B.t.u. gas together with 33 lbs. of coke from which an additional 1000 cu. ft. of blue water-gas can be produced. Overall conversion costs are somewhat less than those for carburetted water-gas. The production of 945 B.t.u. gas by reforming a light distillate of 32 Bé. in a standard 3-shell water-gas machine has been described by Willien.[59]

According to Frey, Huppke and Guyer,[60] a clean fuel gas from hydrocarbons such as propane and butane is obtained by the following procedure: A mixture of steam and hydrocarbons is passed through a series of externally-heated catalyst masses, the gas mixture being preheated between the various stages and hydrocarbon material added at intervals. The catalyst may consist of screens of nickel promoted with alumina. The calorific value of the resultant gas, consisting of mixed gaseous hydrocarbons and water-gas, can be controlled at will.

PRODUCTION OF HYDROCYANIC ACID FROM HYDROCARBONS BY HIGH TEMPERATURE REACTIONS

It has long been known that hydrocyanic acid may be produced by the interaction of hydrocarbons, such as methane, with ammonia at high temperatures and several processes for the manufacture of that material have been developed commercially. It has been shown by Andrussow[61] that good yields of hydrocyanic acid are obtained by passage over platinum gauze at about 1000°C. of a mixture of ammonia, methane and oxygen (or the corresponding amount of air) in proportions corresponding to the equation:—

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[56] T. B. Williams, *Am. Gas Assoc., Proc.*, **1933**, 793; *Chem. Abs.*, 1934, **28**, 4207.

[57] J. A. Perry, U. S. P. 1,939,410, Dec. 12, 1933, to United Gas Improvement Co.; *Brit. Chem. Abs.* **B**, 1934, 869; *Chem. Abs.*, 1934, **28**, 1511; *J. Inst. Pet. Tech.*, 1934, **20**, 112A. See also, H. G. Terzian, U. S. P. 1,980,115, Nov. 6, 1934, to United Gas Improvement Co.; *Chem. Abs.*, 1935, **29**, 324; *Brit. Chem. Abs.* **B**, 1935, 982.

[58] J. A. Perry, *Gas Age-Record*, 1933, 72, 479; *Chem. Abs.*, 1934, **28**, 1505.

[59] L. J. Willien, *Gas Age-Record*, 1933, 72, 431; *Chem. Abs.*, 1934, **28**, 1505.

[60] F. E. Frey, W. F. Huppke and J. A. Guyer, U. S. P. 2,029,657, Feb. 4, 1936, to Phillips Petroleum Co.; *Chem. Abs.*, 1936, **30**, 1981. For a description of the apparatus and operating details, see F. E. Frey, W. F. Huppke and J. A. Guyer, U. S. P. 2,029,317, Feb. 4, 1936, to Phillips Petroleum Co.; *Chem. Abs.*, 1936, **30**, 1981.

$$2NH_3 + 3O_2 \text{ (or 14.4 air)} + 2CH_4 \longrightarrow 2HCN + 6H_2O + 230 \text{ kg. cal.}$$

With these proportions of reactants at 1000°C., 58-63 per cent of the ammonia is converted into hydrocyanic acid, about 8-12 per cent to nitrogen and about 26-30 per cent remains undecomposed. The methane is partly transformed into hydrocyanic acid and partly into a mixture of hydrogen and carbon monoxide. A small excess of either ammonia or methane is not harmful but with increasing amounts of methane most of the oxygen is consumed in the formation of carbon monoxide and hydrogen, thus decreasing the yields of hydrocyanic acid. A decreased yield of this acid is also obtained on addition of carbon monoxide to the reaction mixture. Oxidation of ammonia to nitric oxide and, in the presence of methane and other hydrocarbons, to hydrocyanic acid is considered by Andrussow to be a distinct catalytic process taking place in the immediate proximity of the catalyst surface with such rapidity that the intermediate steps can only be followed under very special experimental conditions. In some instances nitric oxide may be substituted for ammonia.[62] A 97 per cent platinum-3 per cent indium alloy gauze also has been suggested for this reaction under about the same conditions.[63]

Another method for preparing hydrogen cyanide comprises conducting ammonia (1 vol.), methane (2-5 vol.) and oxygen (3 vol.) through a silica tube heated to 1300°C.[64] Wood charcoal may be employed as a contact agent.[65] Mixtures of methane and ammonia have been reported to be transformed to hydrogen cyanide in recuperation furnaces under reduced pressure.[66] When temperatures of 500°C. or higher are necessary, it is suggested that the apparatus be made of or lined with aluminum oxide free from silicates.[66a]

Condensation of unsaturated hydrocarbons with ammonia, or substituted ammonias, is known to yield amines under certain conditions, particularly in the presence of catalysts and at relatively low temperatures.[67] However, Egloff and Schaad[68] report the production of amines by the direct combination of noncondensable hydrocarbon gases (from cracking operations) with ammonia at about 650°C. and under pressures ranging from 1000 lbs. per sq. in. to subatmospheric pressures.

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[61] L. Andrussow. *Angew. Chem.*, 1935. **48**, 593; *Chem. Abs.*, 1935. **29**, 8244; *Brit. Chem. Abs.* **A**, 1935, 1329; *J. Inst. Pet. Tech.*, 1935, **21**, 415A.

[62] French P. 781,239, May 11, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 6373. See also, H. A. Bond and C. R. Harris, French P. 795,092, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936. **30**, 5374.

[63] British P. 451,609, 1936, addn. to 361,004, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, **27**, 1100; 1937, **31**, 510; *Brit. Chem. Abs.* **B**, 1932, 101; **B**, 1936, 1206.

[64] P. J. Carlisle and A. D. Macallum, British P. 442,737, 1936, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1936, 493; *Chem. Abs.*, 1936, **30**, 5003. U. S. P. 2,069,545, Feb. 2, 1937.

[65] British P. 441,632, 1936, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1936, 493; *Chem. Abs.*, 1936, **30**, 4631.

[66] French P. 790,851, 1935, to Ruhrchemie A.-G.; *Chem. Abs.*, 1936, **30**, 2985. See also H. Tramm, German P. 630,767, 1936, to Ruhrchemie A.-G.; *Chem. Abs.*, 1937, **31**, 223.

[66a] German P. 636,011, 1936, to Ruhrchemie A.-G.; *Chem. Abs.*, 1937, **31**, 580.

[67] This condensation is described in greater detail in Chapter 24.

[68] G. Egloff and R. E. Schaad, U. S. P. 1,973,474, Sept. 11, 1934, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1935, 759; *Chem. Abs.*, 1934, **28**, 6997.

Chapter 11

Direct Hydration of Olefins to Alcohols

The direct addition of water to olefin hydrocarbons according to the general equation

$$C_nH_{2n} + H_2O \longrightarrow C_nH_{2n+1}OH$$

would appear to offer possibilities for the commercial synthesis of alcohols. The simplicity of the reaction, as compared with the well-established although indirect methods involving absorption in sulphuric acid, has attracted a large number of investigators.[1] Consideration of the thermodynamics involved has shown that hydration is favored by low temperatures and high pressures. Consequently good yields, which are essential to the industrial success of the process, can be attained only in the presence of catalysts capable of effecting rapid combination at relatively low temperatures.[2]

ETHYLENE

Investigations on the hydration of this olefin have been devoted for the most part to the discovery of contact agents which can fulfill the conditions mentioned above. Several types have been employed and for purposes of classification they may be listed as:

1. Organic catalysts, such as pyridine or quinoline.
2. Inorganic catalysts.
    a. Solutions of acids, e.g., sulphuric or phosphoric.
    b. Acidic salts, as for example, acid phosphates.
    c. Oxide catalysts, as alumina or clays.

Aqueous solutions of nitrogen bases (pyridine or quinoline) or their salts were proposed by Bent and Wik.[3] These are reported applicable to the hydration of ethylene or propene at temperatures below 350°C. and pressures of about 3,000 lbs. per sq. in.

Dilute Mineral Acids as Catalysts. The use of dilute mineral acids has been suggested by many investigators. Dreyfus[4] recommended sulphuric acid of 2 to 10 per cent concentration when operations are carried out under pressure at 150° to 300°C. Higher concentrations, 15 to 60 per cent, of either sulphuric or phosphoric acid are advocated by Metzger.[5] The contact agents may be absorbed on an inert carrier, such as pumice or silica gel, and many contain dissolved silver or lithium sulphate. According to Balcar,[6] any catalyst which is lost during hydration of the olefin may be replaced by the gradual addition of ethyl sulphate. Complete separation of alcohol from ethylene may be accomplished by scrubbing under pressure with water.[7]

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[1] See, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[2] The economic aspect of the synthesis of alcohols has been discussed by N. Parrarano (*Giorn. Chim. Appl.*, 1934, **16**, 425; *Brit. Chem. Abs.* **B**, 1934, 1093; *Chem. Abs.*, 1934, **28**, 5803). The equilibria involved in the hydration of olefins are of interest because their study should contribute materially to knowledge of the energy relationships of the olefin hydrocarbons.

[3] F. A. Bent and S. N. Wik. U. S. P. 2,036,317, Apr. 7, 1936; *Chem. Abs.*, 1936, **30**, 3429.

[4] H. Dreyfus, U. S. P. 2,045,842, June 30, 1936; *Chem. Abs.*, 1936, **30**, 5588.

[5] F. J. Metzger, U. S. P. 2,050,442, 2,050,443 and 2,050,445, Aug. 11, 1936, to Air Reduction Co.; *Chem. Abs.*, 1936, **30**, 6725. British P. 408.006 and 408.203. 1934; *Chem. Abs.*, 1934, **28**, 5474, 5475; *Brit. Chem. Abs.* **B**, 1934, 492, 568; *J. Inst. Pet. Tech.*, 1934, **20**, 378A. An apparatus

One continuous process comprises contacting the olefin, under a pressure of about 100 atmospheres, with a countercurrent stream of dilute (1 to 10 per cent) aqueous sulphuric acid.[8] The temperature should not exceed 350°C. and the pressure should be sufficiently great to prevent substantial evaporation of the alcohol formed. Concentration of the acid liquor is suppressed by the continual addition of water vapor. After withdrawal of the dilute acid from the reaction zone, it is subjected to distillation (to recover alcohol) and then recirculated.

The formation of ethers during hydration of olefins has been observed by many investigators. Shiffler and Holm[9] noted that the development of such oxygen-containing compounds could be controlled by operating at 120° to 150°C. and 15 to 100 pounds pressure, using 20 to 80 per cent sulphuric acid as the contact agent. Furthermore, after separation of alcohol and ether, recycling of the latter is said to aid in the inhibition of its production.

As previously mentioned, the sulphates of silver or lithium may be employed as promoters. Other metallic sulphates which may be used similarly include those of beryllium, magnesium, zinc, cadmium, aluminum, manganese, chromium, cobalt or nickel.[10] It has been suggested also that the reaction vessel be lined with a metal (such as copper or a copper alloy) which has an electrochemical potential, compared with hydrogen, between +0.2 and −0.4 volts.[11]

Gilliland, Gunness and Bowles[12] used dilute aqueous sulphuric acid (about 3 mole per cent) in determining the equilibrium constants for the hydration of ethylene at 176-307°C. under pressures ranging from 80 to 260 atmospheres. They found that the values for free energy and the equilibrium constant at 200 atmospheres pressure differed by about 10 per cent when calculated from the partial pressures of the reactants and from their fugacities.[13] The explanation offered was that ethylene behaves almost as a perfect gas while deviations of ethanol and steam from the ideal gas laws tend to compensate one another. Polymerization of ethylene was a side reaction above 250°C. and 200 atmospheres pressure, and ether formation at temperatures below 220°C. These investigators found that the following equation expressed the relation between free energy change and temperature in the range studied:

$$\Delta F^\circ = -7780 + 26.2T$$

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for carrying out hydration under 100 to 1,000 pounds pressure is described by F. J. Metzger, U. S. P. 2,021,564, Nov. 19, 1935, to Air Reduction Co.; *Chem. Abs.*, 1936, **30**, 485. British P. 402,613, 1933; *Chem. Abs.*, 1934, **28**, 2723; *Brit. Chem. Abs.* B, 1934, 232; *J. Inst. Pet. Tech.*, 1934, **20**, 192A. French P. 749,478, 1933; *Chem. Abs.*, 1934, **28**, 777. German P. 622,267, 1935; *Chem. Abs.*, 1936, **30**, 1384.

[6] F. R. Balcar, U. S. P. 2,044,417, June 16, 1936, to Air Reduction Co.; *Chem. Abs.*, 1936, **30**, 5236.

[7] W. Wilkinson, U. S. P. 2,044,414, June 16, 1936, to Air Reduction Co.; *Chem. Abs.*, 1936, **30**, 5236.

[8] British P. 446,781, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 6758; *J. Inst. Pet. Tech.*, 1936, **22**, 296A. French P. 786,081, 1935; *Chem. Abs.*, 1936, **30**, 1085.

[9] W. H. Shiffler and M. M. Holm, U. S. P. 1,951,740, Mar. 20, 1934, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1934, **28**, 3415; *Brit. Chem. Abs.* B, 1935, 138.

[10] See, Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, 1934.

[11] French P. 786,687, 1935, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 730. See also, British P. 433,868, 1935; *Brit. Chem. Abs.* B, 1935, 938. F. A. Bent and R. W. Millar, British P. 453,147, 1935, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* B, 1936, 1141; *J. Inst. Pet. Tech.*, 1936, **22**, 515A; *Chem. Abs.*, 1937, **31**, 1036.

[12] E. R. Gilliland, R. C. Gunness and V. O. Bowles, *Ind. Eng. Chem.*, 1936, **28**, 370; *Chem. Abs.*, 1936, **30**, 3307; *Brit. Chem. Abs.* A, 1936, 565; *J. Inst. Pet. Tech.*, 1936, **22**, 253A.

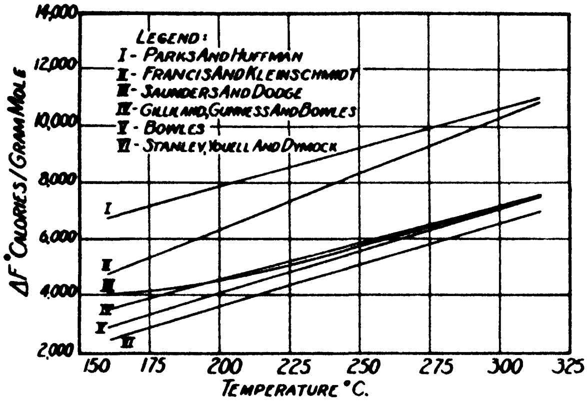
[13] Fugacity is a corrected vapor pressure. For a discussion of such, see Chapter 54.

Bowles[14] conducted a series of liquid-phase hydration experiments at 225° to 325°C. and at pressures of about 400 atmospheres. He recommended the equation

$$\Delta F^\circ = -10{,}120 + 30.2T$$

as representing his results.

The expressions deduced by several investigators are compared graphically in Fig. 90, which shows the different relationships for the variation of free energy change with temperature. The experimental data of Sanders and Dodge,[15] of Bowles,[16] of Stanley, Youell and Dymock[17] and of Gilliland, Gunness and Bowles[18] are in good agreement, whereas the computed values of Parks and Huffman[19] and of Francis and Kleinschmidt[20] are much higher. In an attempt to correlate all available experimental data on vapor-phase hydration of ethylene, Gilliland and his collaborators suggest the following:



Courtesy Industrial and Engineering Chemistry

FIG. 90.—Comparison of Results of Various Investigators on Relationship of Temperature and Free Energy of Vapor-phase Hydration of Ethylene. (E. R. Gilliland, R. C. Gunness and V. O. Bowles)

$$\Delta F^\circ = 26.9T - 8300$$

Acidic Salts as Catalysts. Some of the more important members of this group are the acid phosphates of which a large number have been described. Joshua, Stanley and Dymock have suggested the acid orthophosphates of uranium, boron,[21] ferrous iron,[22] cobalt,[23] copper,[24] and manganese.[25] These contact agents may be employed as granules, supported on an inert carrier or in solution for operations effected at temperatures between 100° and 300°C. and at pressures below 250 atmospheres. One method of preparation comprises dissolving the metallic oxide in an aqueous solution of phosphoric acid, the latter being slightly in excess, and evaporating to dryness. The residue is then baked and subsequently formed into tablets or pellets. The mechanical stability of these particles may be improved by incorporation of various binding agents including drying oils such as tung or linseed oil,[26] non-drying vegetable oils (e.g., rape or castor), animal oils and high-molecular weight aliphatic alcohols, acids, ketones, ethers or anhydrides.[27] Many water-soluble substances, as for example, glycerol, mannitol, pectin, gelatin, starch and sucrose, have been suggested also as stabilizing agents.[28]

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[14] V. O. Bowles, M. S. Thesis, Mass. Inst. Tech., 1933.

[15] Using oxide catalysts: F. J. Sanders and B. F. Dodge, *Ind. Eng. Chem.*, 1934, **26**, 208; *Brit. Chem. Abs.* **B**, 1934, 392; *Chem. Abs.*, 1934, **28**, 2171.

[16] V. O. Bowles *(loc. cit.)* used dilute mineral acids.

[17] H. M. Stanley, J. E. Youell and J. B. Dymock, *J.S.C.I.*, 1934, **53**, 205T; *Chem. Abs.*, 1934, **28**, 6362; *Brit. Chem. Abs.* **A**, 1934, 1070. Phosphate catalysts were employed.

[18] E. R. Gilliland, R. C. Gunness and V. O. Bowles *(loc. cit.)* used mineral acids.

[19] G. S. Parks and H. T. Huffman, "The Free Energies of Some Organic Compounds." The Chemical Catalog Co., Inc., New York, 1932.

[20] A. W. Francis and R. V. Kleinschmidt, *Amer. Petroleum Inst., Proc. 10th Ann. Meeting*, 1930, **11**, Sect. III, 93; *Chem. Abs.*, 1930, **24**, 2369.

[21] W. P. Joshua, H. M. Stanley and J. B. Dymock, U. S. P. 1,978,266, Oct. 23, 1934 to Distillers Co. Ltd.; *Chem. Abs.*, 1935, **29**, 180. See also, Dutch P. 63,943, 1933; *J. Inst. Pet. Tech.*, 1935, **21**, 176A. Austrian P. 141,030, 1934; *J. Inst. Pet. Tech.*, 1935, **21**, 224A.

[22] W. P. Joshua, H. M. Stanley and J. B. Dymock, U. S. P. 1,978,267, Oct. 23, 1934, to Distillers Co. Ltd.; *Chem. Abs.*, 1935, **29**, 180.

In addition to the phosphates previously mentioned, Joshua, Stanley and Dymock[29] have proposed also catalysts composed of complex boro-phosphates of copper, iron, or nickel, as well as those of calcium, strontium, barium or magnesium.[30] Some of the results obtained with these contact agents are summarized in Table 57.

TABLE 57.—*Hydration of Ethylene Using Acid Phosphate Catalysts.*

Catalyst Composition	Press. (atms.)	Temp. °C.	Molar Ratio $C_2H_4:H_2O$	Gas Velocity[a]	Alcohol g. per hr. per l. of catalyst	Per cent yield per pass
Uranyl oxalate $+2.3H_3PO_4$	20	270	4:1	4,000	30.3	0.37
$FeO \cdot 2.5H_3PO_4$	20	270	4.1	4,000	67.8	0.83
$FeO \cdot 2.5H_3PO_4$	40	280	7:1	12,600	174	0.67
$CoO \cdot 2.5H_3PO_4$	20	270	4:1	4,000	31 8	0.38
$CuO \cdot 2.0H_3PO_4$	20	270	4:1	4,000	70.9	0.85
$CuO \cdot 2.0H_3PO_4$	40	300	5.4:1	12,000	221	1.12
$MnO \cdot 2.7H_3PO_4$	20	250	3:1	2,000	38	0.94
$MnO \cdot 2.7H_3PO_4$	30	250	5 6:1	2,000	42.7	1.04
$CuO \cdot MnO \cdot 4H_3PO_4$	20	270	4 1:1	4,000	79 1	0.97
$CuO \cdot 1.5MnO \cdot 6.05H_3PO_4$	20	270	3 8:1	4,000	88.5	1.06
$0.5B_2O_3 \cdot FeO \cdot 3.67H_3PO_4$	20	270	3 4:1	4,000	66.9	
$0.5B_2O_3 \cdot MnO \cdot 3.6H_3PO_4$	20	280	2.3:1	4,000	101.9	...
$CaO \cdot 0.5B_2O_3 \cdot 3.6H_3PO_4$	20	280	2.3:1	4,000	107	1.15
$CaO \cdot 0.5B_2O_3 \cdot 3.6H_3PO_4$	40	290	3:1	12,000	467	1.70
$BaO \cdot 0.5B_2O_3 \cdot 3.6H_3PO_4$	20	280	2 3:1	4,200	74	..
$BaO \cdot 0.5B_2O_3 \cdot 3.6H_3PO_4$	40	290	3:1	12,500	250	...
$SrO \cdot 0.5B_2O_3 \cdot 3.6H_3PO_4$	40	290	3:1	12,500	207	...
$MgO \cdot 0.5B_2O_3 \cdot 3.6H_3PO_4$	20	280	2 3:1	4,450	46.4	....
$B_2O_3 \cdot 2.2H_3PO_4$	20	270	4:1	4,000	37.0	0.44

[a] Liters of ethylene under standard conditions. The volume of catalyst was 100 cc.

Using 100 cc. of a catalyst of the composition $MnO \cdot 0.5B_2O_3 \cdot 2.8H_3PO_4$, Joshua, Stanley and Dymock[31] investigated the effect of change in ethylene-steam ratio

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[23] W. P. Joshua, H. M. Stanley and J. B. Dymock, U. S. P. 1,978,268, Oct. 23, 1934, to Distillers Co. Ltd.; *Chem. Abs.*, 1935, **29**, 180.

[24] W. P. Joshua, H. M. Stanley and J. B. Dymock, U. S. P. 1,978,269, Oct. 23, 1934, to Distillers Co. Ltd.; *Chem. Abs.*, 1935, **29**, 180.

[25] W. P. Joshua, H. M. Stanley and J. B. Dymock, U. S. P. 1,978,270, Oct. 23, 1934, to Distillers Co. Ltd.; *Chem. Abs.*, 1935, **29**, 180.

[26] W. P. Joshua, H. M. Stanley and J. B. Dymock, British P. 404,115, 1934, to Distillers Co. Ltd.; *Chem. Abs.*, 1934, **28**, 3740; *Brit. Chem. Abs.* B, 1934, 274. French P. 762,857, 1934; *Chem. Abs.*, 1934, **28**, 5075.

[27] W. P. Joshua, H. M. Stanley and J. B. Dymock, British P. 422,635, 1935, to Distillers Co. Ltd.; *Chem. Abs.*, 1935, **29**, 4373; *Brit. Chem. Abs.* B, 1935, 262.

[28] W. P. Joshua, H. M. Stanley and J. B. Dymock, British P. 413,043, 1934, to Distillers Co. Ltd.; *Chem. Abs.*, 1935, **29**, 474; *Brit. Chem. Abs.* B, 1934, 823.

[29] W. P. Joshua, H. M. Stanley and J. B. Dymock, U. S. P. 2,009,775, July 30, 1935, to Distillers Co. Ltd.; *Chem. Abs.*, 1935, **29**, 6245.

[30] W. P. Joshua, H. M. Stanley and J. B. Dymock, British P. 415,426, 1934, to Distillers Co. Ltd.; *Chem. Abs.*, 1935, **29**, 811; *Brit. Chem. Abs.* B, 1934, 952. French P. 767,321, 1934; *Chem Abs.*, 1935, **29**, 175. U. S. P. 2,075,203, March 30, 1937.

[31] W. P. Joshua, H. M. Stanley and J. B. Dymock, *loc. cit.*

on the yield of ethanol. Their experiments were carried out at 20 atmospheres pressure and 275° to 290°C., and about 400 liters (under standard conditions) of ethylene per hour were conducted over the contact agent. The results are shown in Table 58.

TABLE 58.—*Effect of Ethylene-Steam Ratio on Yield of Ethanol with a Manganese Boro-Phosphate Catalyst.*

Molar ratio C_2H_4:H_2O	Hourly output of alcohol in grams	Per cent of alcohol in condensate
3.2	7.66	6.30
2.7	8.16	6.32
2.3	9.05	5.53
1.94	9.98	5.50
1.65	10.75	4.83
1.04	13.07	3.47

A study of the equilibrium conditions of the reversible reaction

$$C_2H_4 + H_2O \rightleftharpoons C_2H_5OH$$

was made by Stanley, Youell and Dymock.[32] In this instance also a manganese boro-phosphate catalyst was employed[33] and the temperature range was 175° to 250°C.[34] Only atmospheric pressure was maintained during interaction. Equilibrium was approached from both directions, that is, from synthesis of alcohol from olefin and water and from decomposition of alcohol to olefin and water. The constants were calculated according to the equation

$$K_p = \frac{p_{C_2H_5OH}}{p_{C_2H_4} \times p_{H_2O}}$$

Values of the latter, at different temperatures, are given in Table 59.

TABLE 59.—*Equilibrium Constants (K_p) for the Vapor-Phase Hydration of Ethylene.*

Temp. °C.	K_p From synthesis of ethanol	K_p From decomposition of ethanol	Mean
145	6.2×10^{-2}	7.5×10^{-2}	6.8×10^{-2}
175	3.4×10^{-2}	3.8×10^{-2}	3.6×10^{-2}
200	1.59×10^{-2}	1.7×10^{-2}	1.65×10^{-2}
225	1.06×10^{-2}	1.08×10^{-2}	1.07×10^{-2}
250	6.30×10^{-3}	7.08×10^{-3}	6.7×10^{-3}

As shown in Fig. 91, plotting $\log_{10}K_p$ (as ordinates) and $\frac{10^3}{T}$ (as abscissa) a linear relation between the temperature (T) and the equilibrium constant is obtained. This is of the type

$$y = ax + b$$

in which a has a value of 2.1 and b of −6.195. The relationship between K_p and T, therefore, may be written as

$$\log_{10} K_p = \frac{2100}{T} - 6.195$$

Substitution of 380° for T in the above equation gives a value of 1.06×10^{-8} for

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[32] H. M. Stanley, J. E. Youell and J. B. Dymock, *J.S.C.I.*, 1934, 53, 205T; *Chem. Abs.*, 1934, 28, 6362; *J. Inst. Pet. Tech.*, 1934, 20, 488A; *Brit. Chem. Abs.* A, 1934, 1070.

[33] The composition of this material was $MnO \cdot B_2O_3 \cdot xH_3PO_4$, in which x varied from 2.4 to 3.6.

[34] In experiments at 145°C. the catalyst consisted of pumice impregnated with 66 per cent sulphuric acid containing 5 per cent of silver sulphate.

K_p which is in close agreement with the figure obtained by Saunders and Dodge[35] at the same temperature and 70 atmospheres pressure. Stanley and his collaborators calculated (from their data) the heat of hydration of ethylene to be +9600 calories per mole.

Phosphate catalysts have been used by other workers. Dreyfus[36] recommended alkali or alkaline-earth phosphates, such as sodium metaphosphate. Those of tin, lead, cadmium, boron, strontium, beryllium or zinc have been proposed by Horsley.[37] Various mixtures, such as calcium metaphosphate containing a small proportion of the metaphosphates of barium, calcium, strontium, titanium, chromium or tellurium, have been suggested.[38] Other contact agents, which are said to be especially applicable to high-pressure operations at temperatures of 100° to 300°C., are those comprising 1 to 2 moles of the metaphosphate of a trivalent element, such as aluminum[39] or iron,[40] and one mole of a metaphosphate of a divalent metal such as cadmium, nickel, calcium, lead, zinc, copper or tin.

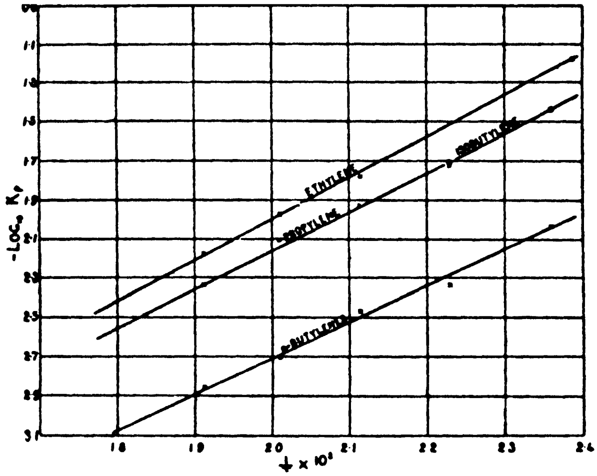

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FIG. 91.—Relationship of Temperature to Equilibrium Constant for Vapor-phase Hydration of Olefins. (H. M. Stanley, J. E. Youell and J. B. Dymock)

As an illustration, Horsley prepared an acid cadmium phosphate by heating together cadmium oxide and phosphorus pentoxide in the correct proportions to give a material having the composition $CdO \cdot 1.5H_3PO_4$. A mixture of steam and ethylene (in the molar ratio of 3:7) was conducted, at 100 atmospheres pressure and 290°C., over the catalyst in such a manner that the time of contact was one minute. A 3.36 per cent conversion (per pass) of ethylene to ethanol was effected. Some results, obtained under the same conditions of temperature and pressure but with different contact agents, are summarized in Table 60.

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[35] See section on oxide catalysts.

[36] H. Dreyfus, U. S. P. 2,020.674, Nov. 12, 1935; *Chem. Abs.*, 1936, **30**, 485. British P. 407.722. 1934; *Chem. Abs.*, 1934, **28**, 5077; *Brit. Chem. Abs.* **B**, 1934, 442; *J. Inst. Pet. Tech.*, 1934, **20**, 336A. French P. 759.661, 1934; *Chem. Abs.*, 1934, **28**, 3415.

[37] G. F. Horsley, U. S. P. 1,977,632, 1,977,633, 1,977,634 and 1,977,635. Oct. 23, 1934, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1935, **29**, 180. See also. British P. 407,944, 1934; *Chem. Abs.*, 1934, **28**, 5080; *Brit. Chem. Abs.* **B**, 1934, 564. French P. 761,276, 1934; *Chem. Abs.*, 1934, **28**, 4072.

[38] G. F. Horsley, U. S. P. 2.051,046. Aug. 18. 1936. to Imperial Chemical Industries. Ltd.: *Chem. Abs.*, 1936, **30**, 6765. British P. 423,877, 1935; *Chem. Abs.*, 1935, **29**, 4374; *Brit. Chem. Abs.* **B**, 1935, 347.

[39] G. F. Horsley, U. S. P. 2,015,073, Sept. 24, 1935, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1935, **29**, 7342; British P. 435,769, 1935; *Chem. Abs.*, 1936, **30**, 1383; *Brit. Chem. Abs.* **B**, 1935, 1128.

[40] G. F. Horsley, British P. 408,313, 1934, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1934, **28**, 1468; *Brit. Chem. Abs.* **B**, 1934, 491. U. S. P. 2,064,116, Dec. 15, 1936; *Chem. Abs.*, 1937, **31**, 700.

TABLE 60.—*Catalytic Hydration of Ethylene.*

Composition of catalyst	Space velocity in reciprocal hours[a]	Alcohol output in grams per liter of catalyst	Per cent conversion of C_2H_4 per pass
$CdO \cdot 1.5H_3PO_4$	([b])	243	3.36
$B_2O_3 \cdot 2H_3PO_4$	6000	155	....
$SrO \cdot 2H_3PO_4$	6000	216	2.69
$FeO \cdot Fe_2O_3 \cdot 8H_3PO_4$[c]	([b])	278	3.46

[a] Space velocity expressed as liters of gas at 20°C. and atmospheric pressure passed per hour over 1 liter of catalyst.

[b] Contact time about 1 minute.

[c] Prepared from ferrous oxalate, ferric oxide, and phosphoric acid.

Liquids, suggested for blending with motor fuels, have been made by the simultaneous hydration and polymerization of mixtures of ethylene and propene.[41] Treatment is effected at high pressures and temperatures of 200° to 350°C. For example, passage of a mixture of 88 volumes of cracking gas and 1 volume of steam (under a total pressure of 120 atmospheres) over a boron phosphate catalyst at 300°C. the time of contact being 1 minute, gave the following products: ethyl alcohol, 46 parts, isopropyl alcohol, 4 parts, acetaldehyde, 0.8 part, and oily liquids, 33 parts.

Dreyfus[42] recommends molten salts of an acidic nature as catalysts. Illustrations of these are fused sodium pyrosulphate or zinc chloride. Other contact agents which have been proposed are the salts of boric, molybdic, tungstic, and vanadic acids[43] and the sulphates of heavy metals.[44] Larson[45] found that hydration of ethylene may be effected at 125-300°C. and 25 to 900 atmospheres pressure in the presence of volatile halides (e.g., hydrogen or ammonium chloride) and an absorbent material, such as activated charcoal.

Oxide Catalysts for Hydration of Ethylene. In an attempt to discover a contact agent for the combination of ethylene and steam, Sanders and Dodge[46] investigated a large number of solid catalysts for the vapor-phase dehydrogenation of ethanol at 360°C. The best was alumina, prepared either by treatment of amalgamated aluminum with water or by precipitation from a solution of sodium aluminate with dilute sulphuric acid. A mixture of tungstic acid and alumina (after reduction with carbon monoxide and hydrogen) was very active but deteriorated somewhat with use. Aluminum silicate, ammonium phosphotungstate and tungstic acid showed a high degree of activity but neither aluminum sulphate nor phosphate was active. Phosphoric acid deposited on pumice was initially a good contact agent but soon lost effectiveness owing to volatilization or formation of volatile compounds. Thoria, precipitated from a solution of the nitrate, did not give satisfactory results.

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[41] M. P. Appleby, British P. 403,406. 1933, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1934, **28**, 3562; *Brit. Chem. Abs.* B, 1934, 184; *J. Inst. Pet. Tech.*, 1934, 20, 112A.

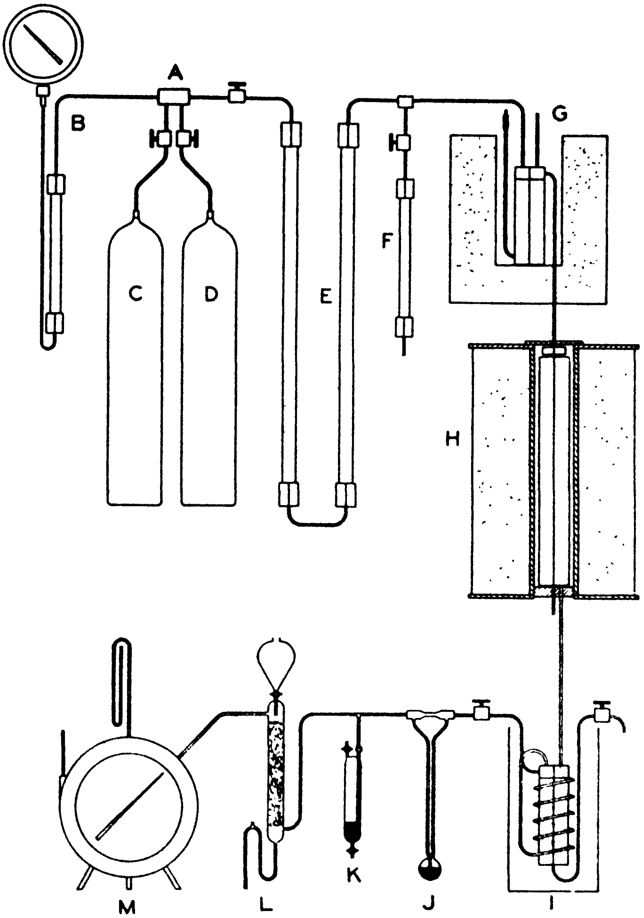
[42] H. Dreyfus, U. S. P. 2,020,672, Nov. 12, 1935; *Chem. Abs.*, 1936, 30, 484.

[43] H. Dreyfus, British P. 408,304, 1932; *Brit. Chem. Abs.* B, 1934, 491; *Chem. Abs.*, 1934, **28**, 5467; *J. Inst. Pet. Tech.*, 1934, **20**, 378A. French P. 43,868, 1934, addition to French P. 745,084; *Chem. Abs.*, 1935, **29**, 1430.

[44] F. A. Bent, Canadian P. 346,722, 1934, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 2546.

[45] A. T. Larson, U. S. P. 2,014,740, Sept. 17, 1935, to E. I. du Pont de Nemours & Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 53A; *Chem. Abs.*, 1935, **29**, 7342; *Brit. Chem. Abs.* B, 1936, 919.

[46] F. J. Sanders and B. F. Dodge, *Ind. Eng. Chem.*, 1934, **26**, 208; *Chem. Abs.*, 1934, **28**, 2171; *J. Inst. Pet. Tech.*, 1934, **20**, 168A; *Brit. Chem. Abs.* B, 1934, 392. *Cf.* L. A. Munro and W. R. Horn, *Canadian J. Research*, 1935, 12, 707.



Courtesy Industrial and Engineering Chemistry

FIG. 92.—Diagram of Apparatus Employed in Catalytic Vapor-phase Hydration of Ethylene. (F. J. Sanders and B. F. Dodge)

A. Coupling
B. Bourdon gage
C. Cylinder
D. Cylinder
E. Purifier
F. Oil trap
G. Water saturator
H. Reactor
I. Condenser and trap
J. Flow indicator
K. Constant-rate sampler
L. Water saturator
M. Flowmeter

The best alumina and tungstic acid catalysts were used by Sanders and Dodge for the hydration of ethylene (by an approximately equimolecular proportion of steam) at pressures of 70 to 135 atmospheres and at temperatures of 360° to 380°C. Under these conditions the corrosive action of water vapor became pronounced and reaction tubes of copper, Monel metal or aluminum failed. However, tubes of

Employment of aluminum oxide as a contact agent is reported by Burda.[49] He prepared a material by precipitation with ammonia from an aqueous solution of ammonium alum, redissolving with a strong alkali (e.g., sodium hydroxide), and reprecipitating from the latter solution by neutralization with sulphuric acid. Other metallic oxides which have been recommended are those of zinc or cadmium with which may be incorporated calcium carbonate, alumina or mercury phosphate.[50]

Strongly basic inorganic substances, such as sodium or potassium hydroxide, have been proposed as catalysts by Dreyfus.[51] van Peski and Langedijk[52] observed the vapor-phase hydration of ethylene at temperatures above 100°C. in the presence of one or more metals which may often serve as dehydrogenating agents. Examples of such are platinum, gold, silver, nickel, cobalt, iron, tungsten or vanadium. Compounds of these, e.g., copper phosphate,[53] a mixture of tungstic acid and iron oxide or gold vanadate,[54] may be employed also.

HYDRATION OF PROPENE

Many of the catalysts which have been mentioned as applicable to the hydration of ethylene are also said to be activating agents for the interaction of steam and propene. For example, Remiz[55] reported a 21 per cent yield of isopropanol by hydration of propene at 110°C. in the presence of 54 per cent sulphuric acid containing 3 per cent of silver sulphate. Aqueous solutions of 15 to 60 per cent concentration of non-volatile inorganic acids (sulphuric or phosphoric) are recommended by Metzger.[56] He proposed to conduct a mixture of olefin and steam at temperatures between 170° and 250°C. and pressures above 100 lb. per sq. in. through the liquid catalyst. At higher pressures (up to about 600 lb. per sq in.), more dilute acid and higher temperatures may be employed. The use of excess steam over that theoretically required is said to avoid formation of isopropyl ether. An example of this procedure is the passage of propene and somewhat more than an equimolecular proportion of steam through 27 per cent sulphuric acid at 200°C. and under a gauge pressure of 250 lbs. A condensate containing 20 per cent isopropyl alcohol was obtained. This was equivalent to about 10 per cent conversion of the olefin per pass. Francis[57] advocates that the molecular ratio of olefin to water be not more than 5:1 when using 60 per cent acid, temperature of about 100°C. and pressures of 300 pounds or higher.

Vapor-phase hydration of propene at 120-150°C. in the presence of 20 to 80 per cent sulphuric acid and at olefin partial pressures up to 100 lb. per sq. in. was suggested by Shiffler and Holm.[58] On the other hand a liquid-phase process has been proposed in which the unsaturated hydrocarbon (under pressure) is continuously contacted with aqueous solutions such as 5 per cent phosphoric acid, 6 to 10 per cent sulphuric acid, 15 to 20 per cent aluminum chloride (hexahydrate) or 50

[49] N. I. Burda, *Coke and Chem. (U.S.S.R.)*, 1932, No. 12, 50; *Chem. Abs.*, 1934, **28**, 2321.

[50] M. Chaffette, French P. 750,053, 1933; *Chem. Abs.*, 1934, **28**, 492.

[51] H. Dreyfus, U. S. P. 1,986,882, Jan. 8, 1935; *Chem. Abs.*, 1935, **29**, 1099.

[52] A. J. van Peski and S. L. Langedijk, U. S. P. 1,999,620, Apr. 30, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 4021.

[53] A. J. van Peski and S. L. Langedijk, U. S. P. 2,055,269, Sept. 22, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 7582.

[54] A. J. van Peski and S. L. Langedijk, U. S. P. 2,057,283, Oct. 13, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 8240.

[55] E. K. Remiz, *J. Appl. Chem. Russ.*, 1936, **9**, 703; *Brit. Chem. Abs.* **A**, 1936, 819; *Chem. Abs.*, 1936, **30**, 7536.

[56] F. J. Metzger, British P. 408,224, 1934 to Air Reduction Co.; *Brit. Chem. Abs.* **B**, 1934, 492; *Chem. Abs.*, 1934, **28**, 5475; *J. Inst. Pet. Tech.*, 1934, **20**, 378A.

[57] A. W. Francis, U. S. P. 2,055,720, Sept. 29, 1936, to Socony-Vacuum Oil Co.; *Chem. Abs.*, 1936, **30**, 8248.

[58] W. H. Shiffler and M. M. Holm, U. S. P. 1,951,740, Mar. 20, 1934, to Standard Oil Co. of Calif.; *Brit. Chem. Abs.* **B**, 1935, 138; *Chem. Abs.*, 1934, **28**, 3415.

per cent zinc chloride, at temperatures up to 350°C.[59] The aqueous catalyst is continuously separated, isopropanol removed therefrom by distillation, and the liquid then recycled.

In addition to silver sulphate, previously mentioned, other salts may be admixed with sulphuric acid. An illustration of such a composition is an aqueous medium containing 8 per cent zinc sulphate and 3 to 5 per cent of the acid with which may be incorporated also the sulphates of calcium, lead or copper.[60] Reaction vessels made of copper or Monel metal are recommended when these liquids are employed. As an example, a mixture of 35 per cent propene and 65 per cent propane is passed, under 3000 lb. per sq. in., at the rate of 3.34 moles (total hydrocarbons) through 2080 cc. of an aqueous catalyst consisting of 4 per cent zinc sulphate and 1.3 per cent sulphuric acid at 285°C. The reported yield of isopropyl alcohol, based on the olefin used, was 12.9 per cent.

Joshua, Stanley and Dymock advocate solid contact agents such as the acid phosphates or boro-phosphates of manganese, copper, iron, cobalt, uranium,[61] calcium, barium, strontium or magnesium.[62] Some of their results are given in Table 61.

TABLE 61.—*Vapor-Phase Hydration of Propene.*

Composition of catalyst	Press. (atm.)	Temp. °C.	Molar ratio $C_3H_6:H_2O$	Gas velocity[a]	Alcohol output Grams per hr. per liter of catalyst	Per cent alcohol in condensate
$MnO \cdot 0.5B_2O_3 \cdot 2.6H_3PO_4$	20	250	11:9	4000	17.95	6.73
$MnO \cdot 0.5B_2O_3 \cdot 2.6H_3PO_4$	20	250	3:1	4000	131.5[b]	10.7
$CaO \cdot 0.5B_2O_3 \cdot 2.6H_3PO_4$	20	260	6:6.5	4000	176[c]	4.75

[a] Liters per hour per liter of catalyst.
[b] Acetone also formed.
[c] Acetone and propanol-1 also formed.

Using a catalyst of the approximate composition $MnO \cdot BO \cdot 2.8H_3PO_4$, the equilibrium conditions (from the standpoint of both synthesis and decomposition) were investigated by Stanley, Youell and Dymock[63] for the reaction

$$C_3H_6 + H_2O \longrightarrow CH_3CHOHCH_3$$

Isopropanol was the main product though small proportions of acetone and *n*-propanol were also formed. Equilibrium constants (K_p) calculated according to the formula

$$K_p = \frac{p_{C_3H_7OH}}{p_{H_2O} \times p_{C_3H_6}}$$

and from data obtained in experiments carried out with gas rates between 8 and 18 liters of propene per hour per liter of catalyst are given in Table 62.

On plotting the logarithms of the mean values of K_p against $\frac{10^3}{T}$ (T being the

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[59] British P. 446,781, 1935, to Standard Oil Development Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 296A; *Chem. Abs.*, 1936, **30**, 6758. French P. 786,081, 1935; *Chem. Abs.*, 1936, **30**, 1065.

[60] British P. 433,868, 1935, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1935, 938; *Chem. Abs.*, 1936, **30**, 731. French P. 786,687, 1935; *Chem. Abs.*, 1936, **30**, 370.

[61] W. P. Joshua, H. M. Stanley and J. B. Dymock, British P. 408,982, 1934, to Distillers Co. Ltd.; *Chem. Abs.*, 1934, **28**, 5468; *Brit. Chem. Abs.* **B**, 1934, 533; *J. Inst. Pet. Tech.*, 1934, **20**, 428A. French P. 766,366, 1934; *Chem. Abs.*, 1934, **28**, 7260. U. S. P. 2,051,144, Aug. 18, 1936; *Chem. Abs.*, 1936, **30**, 6766. U. S. P. 2,075,204, Mar. 30, 1937.

[62] W. P. Joshua, H. M. Stanley and J. B. Dymock, British P. 415,427, 1934, to Distillers Co. Ltd.; *Brit. Chem. Abs.* **B**, 1934, 952; *Chem. Abs.*, 1935, **29**, 811; *J. Inst. Pet. Tech.*, 1934, **20**, 584A.

[63] H. M. Stanley, J. E. Youell and J. B. Dymock, *J.S.C.I.*, 1934, **53**, 205T; *Brit. Chem. Abs.* **A**, 1934, 1070; *J. Inst. Pet. Tech.*, 1934, **20**, 4884; *Chem. Abs.*, 1934, **28**, 6362.

TABLE 62.—*Equilibrium Constants for Vapor-Phase Hydration of Propene.*

Temperature	Values of K_p		
	From synthesis	From decomposition	Mean
175°C.	1.81×10^{-2}	2.00×10^{-2}	1.91×10^{-2}
200°C.	1.16×10^{-2}	1.22×10^{-2}	1.19×10^{-2}
225°C.	7.88×10^{-3}	7.95×10^{-3}	7.92×10^{-3}
250°C.	4.70×10^{-3}	4.57×10^{-3}	4.62×10^{-3}

temperature) a straight line, as shown in Fig. 91, is secured. This linear relation between the equilibrium constant and the temperature may be expressed by the equation:

$$\log_{10} K_p = \frac{1950}{T} - 6.060$$

The heat of hydration of propene, at constant pressure, was computed to be +9000 calories per mole.

A comparison of the data for propene with that for ethylene and the butenes shows that, at a given temperature, equilibrium was less favorable for hydration of propene than for the other olefins. As in the case of ethylene, the best conditions for conversion of propene to propanol-2 are low temperatures and high pressures. Stanley and his collaborators point out that these observations relate only to equilibria and bear no relation to the relative reaction velocities.

Horsley[64] suggested the acid phosphates of boron, beryllium and cadmium as contact agents for operations under pressure and at temperatures of 150° to 300°C. In a process described by Bent and Millar,[65] complete liquefaction of the products of hydration is effected under pressure. The resulting liquid mixture stratifies into an aqueous phase and a hydrocarbon phase. The latter, containing only a small proportion of alcohol, is returned to the reaction zone with more steam. The aqueous layer is removed and subjected to distillation to recover its alcohol content.

HYDRATION OF BUTENES

The work of Marek and Flege[66] on the hydration of butene-2 under 3000 and 5000 pounds pressure in the presence of phosphoric acid on pumice indicated that the main product was butanol-2. The equilibrium constant, K_p, at 482°C. was found to be approximately 2.9×10^{-4}. Stanley, Youell and Dymock[67] have studied the vapor-phase hydration of a mixture of butene-1 and butene-2 using manganese boro-phosphates as catalysts. They also report that butanol-2 was formed from both olefins though a small proportion of butan-2-one and, possibly, butanol-1 was produced. The equilibrium constants for the reaction

$$n\mathrm{C_4H_8} + \mathrm{H_2O} \rightleftharpoons \mathrm{C_2H_5CHOHCH_3}$$

were determined at temperatures of 150° to 250°C. and atmospheric pressure. Stanley and his collaborators assumed that the mixed butenes could be regarded, for practical purposes, as a single compound. The values obtained in these experiments are summarized in Table 63.

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[64] G. F. Horsley, U. S. P. 1,977,633 and 1,977,634, Oct. 23, 1934, to Imperial Chemical Industries Ltd.; *Chem. Abs.*, 1935, **29**, 180.

[65] F. A. Bent and R. W. Millar, U. S. P. 2,010,686, Aug. 6, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 6606.

[66] L. F. Marek and R. K. Flege, *Ind. Eng. Chem.*, 1932, **24**, 1428; *Chem. Abs.*, 1933, **27**, 1189; *Brit. Chem. Abs.* A, 1933, 142. See also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[67] H. M. Stanley, J. E. Youell and J. B. Dymock, *J.S.C.I.*, 1934, **53**, 205T; *Chem. Abs.*, 1934, **28**, 6362; *Brit. Chem. Abs.* A, 1934, 1020; *J. Inst. Pet. Tech.*, 1934, **20**, 488A.

TABLE 63.—*Equilibrium Constants (K_p) for Hydration of n-Butenes.*

Temperature	Values of K_p		
	From synthesis	From decomposition	Mean
150°C.	9.6×10^{-3}	9.2×10^{-3}	9.4×10^{-3}
175°C.	4.54×10^{-3}	4.62×10^{-3}	4.58×10^{-3}
200°C.	3.30×10^{-3}	3.42×10^{-3}	3.36×10^{-3}
225°C.	1.95×10^{-3}	1.98×10^{-3}	1.96×10^{-3}
250°C.	1.36×10^{-3}	1.42×10^{-3}	1.39×10^{-3}

A graph of $\log_{10}K_p$ against $\frac{10^3}{T}$ reveals a linear relationship (see Fig. 91) which can be expressed by the equation

$$\log_{10} K_p = \frac{1845}{T} - 6.395$$

The heat of reaction at constant pressure was calculated to be about +8,450 calories per mole.

It would seem that the equilibrium conversions obtainable in the case of the *n*-butenes should be materially lower than those for ethylene, propene or isobutene under the same conditions. Nevertheless, a 25 per cent yield of butanol-2 by vapor-phase hydration of *n*-butene at 225°C. and 200 atmospheres pressure in the presence of an aqueous catalyst has been reported.[68] The latter consisted of a solution containing 8 per cent zinc chloride and 4.7 per cent sulphuric acid. On the other hand, Joshua and his co-workers found the passage of a mixture of 6 moles of the olefin and 4 moles of steam, under a total pressure of 10 atmospheres, over a solid catalyst having the composition $MnO \cdot 0.5B_2O_3 \cdot 2.6H_3PO_4$[69] or that of $CaO \cdot 0.5B_2O_3 \cdot 2.6H_3PO_4$[70] gave only a 0.3 per cent yield of alcohol per pass. In the latter instances the temperature was 240°C. and the gas rate was 4000 liters (measured under standard conditions) per hour per liter of catalyst.

Hydration of Isobutene. It is well known that isobutene (2-methylpropene) can be hydrated to the corresponding alcohol (2-methylpropanol) under milder conditions than are required with the *n*-butenes.[71] For example, dilute nitric acid is a sufficiently active catalytic agent for the iso-olefin but not for the other unsaturated hydrocarbons.

Lucas and Eberz[72] investigated the rate of hydration of isobutene by this acid. They report that it is increased if potassium nitrate is present also. Some of the data obtained are shown in Table 64. For the reaction

$$(CH_3)_2C{=}CH_2 + H_2O \longrightarrow (CH_3)_3COH$$

these workers define the specific reaction constant k by the equation

$$2.3026 \log_{10} (C_o/C_t) = kt$$

in which C_o is the initial concentration (in moles) of the olefin and C_t the concentration after time t (expressed in hours).

It is evident that if $\log_{10}(C_o/C_t)$ be plotted against t, the slope of the curve will be the constant k. The curves (plotted in this manner) for data secured on the

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[68] British P. 433,868, 1935, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, 30, 731; *Brit. Chem. Abs.* B, 1935, 938.

[69] W. P. Joshua, H. M. Stanley and J. B. Dymock, U. S. P. 2,052,095, Aug. 25, 1936, to Distillers Co. Ltd.; *Chem. Abs.*, 1936, 30, 6761. British P. 408,982, 1934; *Brit. Chem. Abs.* B, 1934, 533; *J. Inst. Pet. Tech.*, 1934, 20, 428A.

[70] W. P. Joshua, H. M. Stanley and J. B. Dymock, British P. 415,427, 1934, to Distillers Co. Ltd.; *Brit. Chem. Abs.* B, 1934, 952; *Chem. Abs.*, 1935, 29, 811; *J. Inst. Pet. Tech.*, 1934, 20, 584A.

[71] A. Butterow, *Ber.*, 1875, 8, 1683; *Chem. Zentr.*, 1876, 1, 147.

[72] H. J. Lucas and W. F. Eberz, *J.A.C.S.*, 1934, 56, 460; *Brit. Chem. Abs.* B, 1934, 369; *Chem. Abs.*, 1934, 28, 1657.

TABLE 64.—*Hydration Constants of Isobutene at 25°C. (± 0.05°C.).*

HNO_3 (Normality)	k	HNO_3 (Normality)	KNO_3 (Normality)	Ionic Strength*	k
0.0500	0.0667	0.0500	0.950	1.000	0.118
0.1005	0.140	0.100	0.900	1.000	0.210
0.2475	0.368	0.250	0.750	1.000	0.520
0.498	0.828	0.498	0.500	0.998	1.070
1.000	2.143	0.498	1.000	1.498	1.367

* H. S. Harned ("The Electrochemistry of Solutions" in H. S. Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., New York, 1930) has defined ionic strength, μ, by the equation

$$\mu = \frac{\sum_{1}^{s} m_i z_i^2}{2}$$

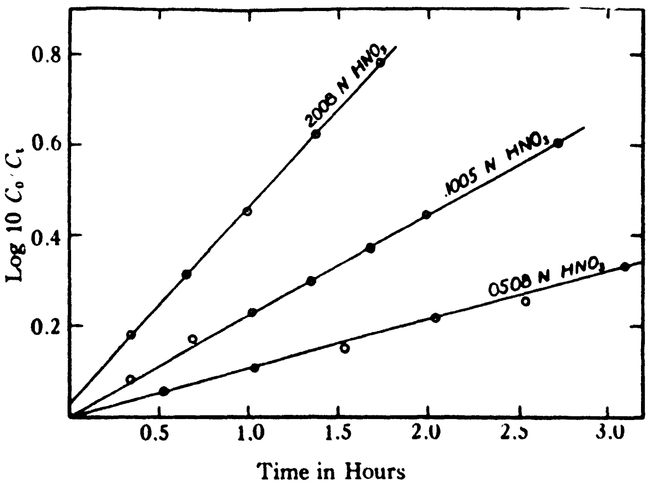
in which m_i and z_i are, respectively, molal concentration and valence of the ion i, and the summation is for all of the ions in solution.

hydration of isobutene at 35°C. are shown in Fig. 93. In Table 65 are given the values of the specific reaction constants at 35°C. ($k_{35°}$) together with the ratio $k_{35°}/k_{25°}$, i.e., the temperature coefficient, and the heats of activation.

TABLE 65.—*Hydration Constants of Isobutene at 35°C. (± 0.05°C.).*

HNO_3 (Normality)	$k_{35°}$	$k_{35°}/k_{25°}$	Heat of activation (kg. cal.)
0.0508	0.244	3.60	23.37
0.1005	0.511	3.64	23.57
0.2008	1.026	3.57	23.22
			Mean 23.39

In addition to potassium nitrate, Lucas and Eberz studied the effect of other salts such as lead, cadmium, zinc and mercuric nitrates, copper and nickel sulphates, and manganese chloride. None of these exerted any beneficial influence except mercuric nitrate. In the presence of the latter the solubility of isobutene in dilute



Courtesy Journal of American Chemical Society

FIG. 93.—Time-Concentration Curves for Hydration of Isobutene at 35°C. (H. T. Lucas and W. F. Eberz)

nitric acid was increased and this was attributed to the formation of a complex, $Hg(NO_3)_2 \cdot C_4H_8$. Also, the free or uncombined olefin in solution was hydrated at a slightly greater rate. Similar observations have been made also with silver nitrate.[72a] That is, the argentic compound and isobutene yielded a complex analogous to that from mercuric nitrate and the olefin, and when this silver derivative was in the acid solution, conversion of the unsaturated hydrocarbon (not in the form of a complex) to alcohol was accelerated.

Eberz and Lucas[73] have measured the equilibrium constants, k_e, for the interaction of 2-methylpropene, $(CH_3)_2CH{=}CH_2$, and water in the liquid phase at 25°C. and 35°C. Their method consisted in dissolving *ter*-butyl alcohol in 0.2N nitric acid and then determining the concentration of unsaturated hydrocarbon and alcohol after at least 24 hours. The values of k_e were found to be 7.48×10^3 (at 25°C.) and 3.9×10^5 (at 35°C.). From these results the free energy change[74] for the reaction

$$C_4H_8(g) + H_2O(1) \longrightarrow C_4H_9OH(1)$$

was calculated as

$$\Delta F^\circ_{298.1} = -1330 \text{ cal. and } \Delta F^\circ_{308.1} = -946 \text{ cal.}$$

Equilibrium between isobutene, trimethyl carbinol and steam in the presence of catalysts of the composition represented by $MnO \cdot BC \cdot 2.4H_3PO_4$ has been studied by Stanley, Youell and Dymock.[75] This was done in two ways: by synthesis of alcohol from olefin and steam, and by decomposition of the alcohol into olefin and water, both operations being conducted at 150° and 175°C. It was observed that the hydrocarbon exhibited a marked tendency to polymerize at temperatures above 180°C. Values of the equilibrium constant (K_p)

$$K_p = \frac{p_{C_4H_9OH}}{p_{C_4H_8} \times p_{H_2O}}$$

are given in Table 66.

TABLE 66.—*Equilibrium Constants for Vapor-Phase Hydration of Isobutene.*

Temperature	From synthesis	From decomposition	Mean
150°C.	3.54×10^{-2}	3.74×10^{-2}	3.64×10^{-2}
175°C.	1.98×10^{-2}	1.98×10^{-2}	1.98×10^{-2}

HIGHER OLEFINS

Little information is available regarding direct hydration of the higher olefins, e.g., pentenes and hexenes. Lucas and Liu[76] effected conversion of 2-methylbutene-2, $(CH_3)_2C{=}CHCH_3$, in the liquid phase at 25° and 35°C., to the corresponding tertiary alcohol employing dilute acids as catalysts. It was observed that reaction proceeded more slowly with this unsaturated hydrocarbon than with 2-methylpropene. However, the rate of reaction was of the first order in both instances. A comparison of the specific reaction constant for these two olefins when using approximately 0.05N nitric acid is shown in Table 67.

[72a] W. F. Eberz, H. J. Welge, D. M. Yost and H. J. Lucas, *J.A.C.S.*, 1937, 59, 45.

[73] W. F. Eberz and H. J. Lucas, *J.A.C.S.*, 1934, 56, 1230; *Brit. Chem. Abs.* A, 1934, 731; *Chem. Abs.*, 1934, 28, 4371.

[74] For a discussion of free energy change, see Chapter 54.

[75] H. M. Stanley, J. E. Youell and J. B. Dymock, *J.S.C.I.*, 1934, 53, 205T; *Chem. Abs.*, 1934, 28, 6362; *J. Inst. Pet. Tech.*, 1934, 20, 488A; *Brit. Chem. Abs.* A, 1934, 1070.

[76] H. J. Lucas and Y. P. Liu, *J.A.C.S.*, 1934, 56, 2138; *Brit. Chem. Abs.* A, 1934, 1312; *Chem. Abs.*, 1935, 29, 113. See also Y. P. Liu and T. C. Wei, *J. Chinese Chem. Soc.*, 1936, 4, 297; *Brit. Chem. Abs. A*, 1936, 1210.

TABLE 67.—*Hydration Rates of 2-Methylpropene and 2-Methylbutene-2.*

Hydrocarbon	HNO_3 (Normality)	$K_{25°}$	$K_{35°}/K_{25°}$	Heat of activation (kg. cal.)
2-Methylpropene	0.0500	0.0667	3.60	23.39
2-Methylbutene-2	0.0532	0.0410	2.83	18.92

Many other acids could be substituted for nitric acid. For concentrations of 0.1M, it was noted that the catalytic activity decreased in the following order: dithionic, sulphuric, hydrochloric, nitric, *p*-toluenesulphonic, picric, oxalic and acetic.

Chapter 12

Direct Esterification of Olefins with Mineral and Organic Acids

The direct combination of olefin hydrocarbons with mineral or organic acids to yield the corresponding alkyl esters is of considerable interest both scientifically and technically. Sulphuric esters, obtained by absorption of olefins in sulphuric acid, constitute important intermediates in the commercial production of the corresponding alcohols. Moreover, alkyl esters of organic acids, such as *sec.*-butyl acetate—normally made by esterification of the alcohol—can be prepared in one stage by treatment of the appropriate olefin with the required organic acid. These addition reactions, many of which are reversible under certain conditions, exhibit interesting features, as, for example, the directive influence of certain solvents or catalysts, especially peroxides, upon the addition of hydrogen bromides to olefins and their derivatives.

According to Markownikov, the addition of halogen acids to olefins tends to occur in such a way that the halogen atom becomes attached to the carbon atom poorer in hydrogen. However, it has for some time been realized that this well-known rule is not rigidly applicable. It has been shown that certain catalysts have a marked influence on the addition of hydrogen bromide to certain olefins, causing the reaction to proceed almost exclusively contrary to the rule of Markownikov. These discoveries, the theoretical implications of which are not yet thoroughly understood, may have an important bearing on the development of modern theories of organic reactions. A brief review of the more recent work along this line is presented under the heading "Peroxide Effect."

ETHYLENE

Reaction with Sulphuric Acid. Ethylene dissolves in concentrated sulphuric acid of about 95-98 per cent concentration at atmospheric pressure (and also in less concentrated acid under increased pressures) to yield both ethylsulphuric acid and diethyl sulphate. The former substance, which is a strong acid, is usually regarded as having the constitution represented by $C_2H_5O—SO_3H$. However, there is evidence for the view that a definite hydrate, $C_2H_5O-SO_3H-H_2O$, exists. Thus, Brooks[1] points out that many of the salts of this acid are hydrated, for example, the barium salt, $Ba(OSO_3—C_2H_5)_2—2H_2O$. Moreover, the reaction velocity between an olefin and 85 per cent sulphuric acid (which undoubtedly contains a substantial proportion of sulphuric acid monohydrate, $H_2SO_4—H_2O$) does not diminish as the reaction proceeds. This fact seems to indicate that there is no increase in the ratio of water to uncombined acid. Brooks also considers that formation of diethyl sulphate probably takes place by interaction of ethylene with hydrated ethylsulphuric acid according to the reversible equation

$$C_2H_5O—SO_3H—H_2O + C_2H_4 \rightleftharpoons (C_2H_5O)_2SO_2 + H_2O$$

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[1] B. T. Brooks, *Ind. Eng. Chem.*, 1935, 27, 278; *Chem. Abs.*, 1935, 29, 2700; *Brit. Chem. Abs.* B, 1935, 536.

The resulting ester is anhydrous. Also, the above equation indicates that an increase in the water content of the reaction mixture should tend to suppress its formation. This conclusion is in agreement with experimental data. Furthermore, the sensible heat of reaction of a monoalkyl sulphate (RO—SO_3H—H_2O) with an olefin is very small compared with the heat of formation of the monoalkyl sulphate.

Concentrated sulphuric acid and ethylene yield a mixture of ethyl hydrogen sulphate and diethyl sulphate. Appreciable amounts of the latter are present when the acid has reacted with about 0.3 mole of the olefin.[2] Large yields of diethyl sulphate are favored by factors assisting solution of the gas in the acid liquor, such, for example, as high partial pressures of ethylene and the employment of concentrated acid. The influence of pressure on the absorption of ethylene in 97.5 per cent sulphuric acid at 80°C. is discussed by Brooks[3] and summarized graphically in Fig. 94. Here it is shown that under 500 lbs. per sq. in. the amount of ethylene absorbed in 40 minutes was 80 per cent of that required for diethyl sulphate formation, whereas at 100 lbs. pressure scarcely 30 per cent was absorbed. Diethyl sulphate formation is sharply suppressed by the use of more dilute sulphuric acid, as is evident from the curves in Fig. 95. In this instance, agitation of ethylene under 450 lbs. pressure with 97.5 per cent acid for 40 minutes yielded over 70 per cent of the theoretical of the dialkyl ester and operation with 93 per cent acid (under similar conditions) furnished only 35 per cent of this ester.

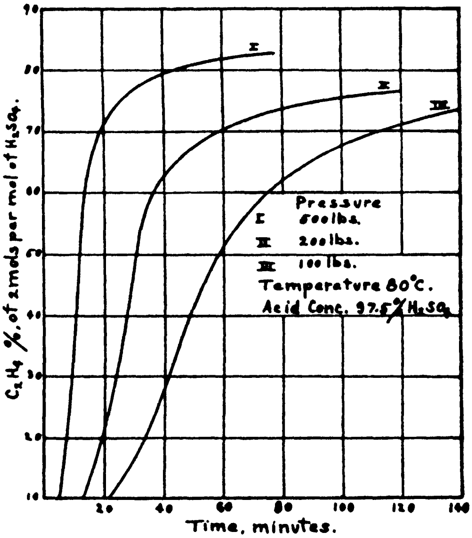

FIG. 94.
Influence of Pressure on Absorption of Ethylene in Sulphuric Acid at 80°C. (B. T. Brooks)

Courtesy Industrial and Engineering Chemistry

Strahler and Hachtel[4] report that 1 kg. of sulphuric acid (d. 1.83) at 70°C. will absorb 400 g. of ethylene, under 15 atmospheres pressure. The products consist of 75 per cent of ethylsulphuric acid and 25 per cent of the dialkyl ester. The latter may be prepared also by heating ethyl hydrogen sulphate under reduced pressure so that the neutral ester is continuously distilled off. This latter step, removal of one of the products, is necessary since the reaction is a reversible one.

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[2] For a discussion of this reaction see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[3] B. T. Brooks, *loc. cit.*

[4] F. Strahler and F. Hachtel, *Brennstoff-Chem.*, 1934, 15, 166; *Brit. Chem. Abs.* B, 1934, 616; *Chem. Abs.*, 1934, 28, 5805.

$$2C_2H_5O{-}SO_3H \rightleftharpoons (C_2H_5O)_2SO_2 + H_2SO_4$$

Dilution with water separates diethyl sulphate from acid liquor as a non-aqueous layer. When recovered sulphuric acid is employed, this simple removal of the product is hindered by suspended carbonaceous material. In such cases water-immiscible solvents, e.g., diethyl ether, have been proposed as extraction agents.[5]

Diethyl sulphate functions as an ethylating agent in many industrial syntheses. Although stable when dry, it undergoes slow hydrolysis in the presence of moisture. For this reason, iron containers to be used for storage or transportation of the ester should be thoroughly dried. Such treatment is particularly recommended by Siebeneicher[6] who investigated an explosion caused by neglect of this precaution.

In one process for producing alkyl esters from olefins and strong acids (such as sulphuric, phosphoric or certain sulphonic acids)[7] the reactants are intimately mixed and simultaneously cooled so as to eliminate the desired products from the reaction zone immediately after formation. For close contact, the components in the liquid state may be passed through a rapidly rotating apparatus.

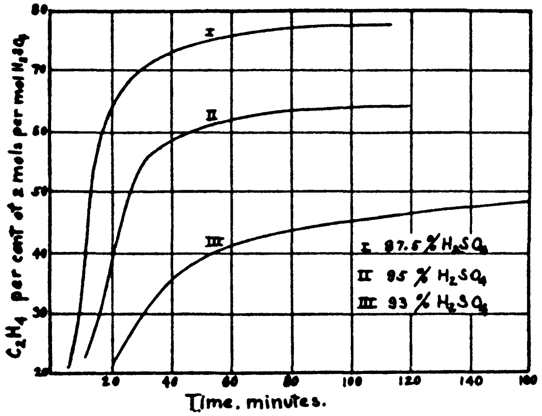

FIG. 95.
Effect of Acid Concentration on Ethylene Absorption under 450 Lb. per Sq. In. Pressure at 50°C. (B. T. Brooks)

Courtesy Industrial and Engineering Chemistry

Reaction with Halogen Acids. Unlike its immediate homologues, ethylene does not appear to combine with the anhydrous halogen acids in the absence of contact agents. For the vapor-phase reaction, sublimed anhydrous aluminum chloride mixed with an equal part of asbestos has been found active, but its catalytic power rapidly declines with use. For example, a 40 per cent conversion of ethylene into ethyl chloride at 80°C. was readily obtained but the catalyst gradually became impregnated with a viscous, syrupy polymerization product which markedly reduced its activity.[8]

Equilibrium constants of the vapor-phase reaction,

$$C_2H_4 + HCl \rightleftharpoons C_2H_5Cl$$

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[5] T. Carruthers, U. S. P. 1,949,366, Feb. 27, 1934; H. L. Cox, U. S. P. 1,949,369, Feb. 27, 1934: both patents to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1934, 28, 2731; *Brit. Chem. Abs.* B, 1935, 13.

[6] K. Siebeneicher, *Angew. Chem.*, 1934, 47, 105; *Chem. Abs.*, 1934, 28, 2908; *Brit. Chem. Abs.* B, 1934, 392.

[7] French P. 755,155, Nov. 21, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, 28, 1357.

[8] A. J. Tulleners, M. C. Tuyn and H. I. Waterman, *Rec. trav. chim.*, 1934, 53, 544; *Chem. Abs.*, 1934, 28, 4035; *Brit. Chem. Abs.* A, 1934, 630.

at 170-230°C. in the presence of bismuth trichloride supported on silica gel have been determined by Rudkovskii, Trifel and Frost.[9] The variation with absolute temperature of the observed equilibrium constant,

$$K_p = \frac{p_{\mathrm{HCl}} \times p_{\mathrm{C_2H_4}}}{p_{\mathrm{C_2H_5Cl}}}$$

could be expressed as follows:

$$\log K_p = 4.96 - \frac{2925}{T}$$

From this equation the heat of reaction was calculated as 13.4 cal. per mole. Activation-energy calculations, carried out by Sun and Liu,[10] show that the reactivities of the hydrogen halides with respect to ethylene increase in the same order as their molecular weights. These findings are said to be in agreement with experimental results.

For combining olefins with halogen hydrides special types of catalysts developed by Strange and Kane are:

(1) An adsorptive material having a microporous structure (such as active carbon or silica gel);[11]
(2) Adsorptive metal-oxide gels (prepared by partially dehydrating a hydrogel or gelatinous precipitate);[12]
(3) A porous catalyst mixed with a heat-absorbing material (such as a mixture of silica gel, hydrated alumina and iron turnings.[13]

When using these activators, the mixture of gases is passed over them at temperatures up to the boiling point of the product. The resultant alkyl halide is recovered by distillation of the products; this may be carried out under reduced pressure.

Reilly[14] employs an anhydrous liquid medium such as ethyl chlorosulphonate (which may also contain bismuth chloride) to effect addition of gaseous ethylene and hydrogen chloride at 40-70°C. Liquid catalysts, such as a solution of ferric chloride in ethyl chloride, or of aluminum chloride in nitrobenzene, have been suggested for this vapor-phase reaction.[15]

Hjerpe and Gruse[16] produce ethyl chloride by passing the reaction mixture at atmospheric pressures over aluminum chloride or bismuth trichloride. For example, refinery or cracking gas is fractionated under pressure and the low boiling cut, containing mainly methane, ethylene (about 10 per cent) and ethane is mixed with hydrogen chloride. The resulting composition should contain approximately equal volumes of olefin and hydrogen halide. This is heated to 350°F. and conducted over aluminum chloride, the time of contact being about 1 to 2 minutes. Ethyl chloride is recovered by scrubbing the gases with a relatively non-volatile petroleum absorbent oil from which it is afterwards separated by distillation. Zinc halides distributed on a supporting medium have been proposed also.[17] Balandin and Livanova[18] obtained a 62 per cent yield of the ester using barium chloride as the contact agent. They observed no reaction at temperatures below 210°C., although above 300°C. dissociation of ethyl chloride occurred.

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[9] D. M. Rudkovskii, A. G. Trifel and A. V. Frost, *Ukrain. Khem. Zhur.*, 1935, **10**, 277; *Chem. Abs.*, 1936, **30**, 2082; *Brit. Chem. Abs.* A, 1936, 159.

[10] C. E. Sun and C. Liu, *J. Chinese Chem. Soc.*, 1936, 4, 98; *Chem. Abs.* 1936, **30**, 7980.

[11] E. H. Strange and T. Kane, British P. 353,032, 1931; *Brit. Chem. Abs.* **B**, 1931, 1085. French P. 709,829, 1931; *Chem. Abs.*, 1932, 26, 997.

[12] E. H. Strange and T. Kane, British P. 414,766, 1933; *Brit. Chem. Abs.* **B**, 1934, 920. French P. 769,103, Aug. 20, 1934; *Chem. Abs.*, 1935, **29**, 478.

[13] E. H. Strange and T. Kane, British P. 435,858, 1935; *Brit. Chem. Abs.* **B**, 1935, 1129. French P. 787,340, 1935; *Chem. Abs.*, 1936, **30**, 1392.

[14] J. H. Reilly, U. S. P. 2,031,228, Feb. 18, 1936, to Dow Chemical Co.; *Chem. Abs.*, 1936, **30**, 2205.

[15] French P. 780,057, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 5862.

[16] E. B. Hjerpe and W. A. Gruse, U. S. P. 1,944,839, Jan. 23, 1934, to Gulf Refining Co.; *Chem. Abs.*, 1934, **28**, 2174; *Brit. Chem. Abs.* B, 1934, 920.

[17] British P. 448,269, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1936, 780; *J. Inst. Pet. Tech.*, 1936, **22**, 369A. French P. 793,770, 1936; *Chem. Abs.*, 1936, **30**, 4515.

Alkyl halides may be prepared also by conducting the gaseous mixture of olefin and hydrogen halide countercurrent to an aqueous solution of a metallic halide, such as antimony or bismuth trichloride. (See Fig. 96.) The alkyl halide is subsequently recovered from the solution of catalyst, which is continuously recycled.[19] It is reported that in this method of operation the concentration of the metallic halide may be so adjusted that olefins may be selectively absorbed from gaseous mixtures, those of higher molecular weight being removed first. To illustrate, cracking gas was mixed with 5 per cent more hydrogen chloride than required theoretically to combine with the olefins present. The gases were then conducted through four consecutive towers countercurrent to the streams of catalysts which were 45, 75, 90 and 95 per cent solutions, respectively, in concentrated hydrochloric acid. The temperature in the first three towers was 25°C. and in the last one was 55°C.; each of the former was followed by a trap maintained at 0°C. The products obtained from each unit (tower and trap), in order of increasing concentration of catalyst, were as follows: (a) almost pure amyl chloride; (b) amyl, butyl and propyl chlorides in the ratio 12:21:8, by weight; (c) these same chlorides, but in the ratio 5:19:8; and (d) butyl and propyl chlorides in the ratio 21:15. Ethylene was the only olefin in the residual gas.

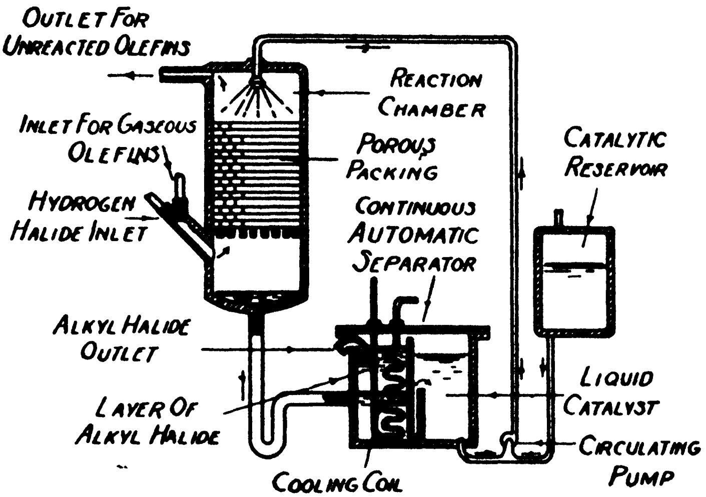

FIG. 96.—Sketch of Method for Preparation of Alkyl Halides with Metallic Halide Catalysts. (H. S. Nutting, P. S. Petrie, D. H. Croope and M. E. Huscher)

According to Tulleners, Tuyn and Waterman,[20] combination of ethylene with hydrogen chloride takes place rapidly and almost quantitatively at −80°C. in the presence of aluminum chloride suspended in ethyl chloride as a diluent. Under these conditions, the olefin is quickly absorbed at normal pressure with practically no formation of by-products. The reaction is virtually carried out in the liquid phase. Using ethylene at atmospheric pressure, a decrease in reaction velocity was noted on raising the temperature to —40°C. and practically no combination took place at —15°C.

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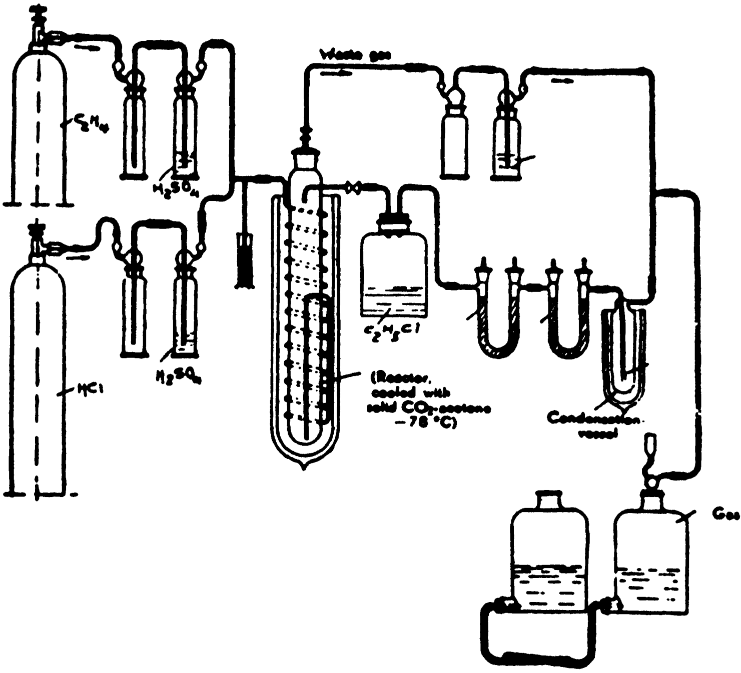
[18] A. Balandin and O. Livanova, *Uchenuie Zapiski (Moscow State Univ.)*, 1934, 2, 237; *Chem. Zentr.*, 1935, 2, 1528, *Chem. Abs.*, 1936, 30, 6321.

[19] H. S. Nutting, P. S. Petrie, D. H. Croope and M. E. Huscher, U. S. P. 1,985,457, Dec. 25, 1934, to Dow Chemical Co.; *Chem. Abs.*, 1935, 29, 1102; *Brit. Chem. Abs.* B, 1935, 1084.

[20] A. J. Tulleners, M. C. Tuyn and H. I. Waterman, *Rec. trav. chim.*, 1934, 53, 544; *Chem. Abs.*, 1934, 28, 4035; *Brit. Chem. Abs.* A, 1934, 630.

Working on a small scale, the best results were obtained using the apparatus sketched in Fig. 97. Ethylene and hydrogen chloride gases, after drying with concentrated sulphuric acid, are mixed and passed through a precooling spiral coiled around the reaction tube which is cooled, as indicated, in a paste of solid carbon dioxide and acetone.[21] The gases, entering the reaction vessel just above the bottom, come in contact with a mixture of aluminum chloride and ethyl chloride. After the discharge of air from the reaction tube, the level of the liquid gradually rises and the product can be run off into a receiver. Gentle warming (not above 12.6°C., the boiling point of ethyl chloride) liberates dissolved gases, from which hydrogen chloride is extracted by soda lime, and ethyl chloride is further recovered in the condenser (cooled to —78°C.). Large gas bottles at the end of the system take care of waste gases and unused ethylene. (The ethylene supply contained 92.6 per cent ethylene, with no higher olefins present.)



Courtesy Recueil des Travaux chimiques des Pays-Bas

FIG. 97.—Apparatus for Reaction of Ethylene and Hydrogen Chloride. (A. J. Tulleners, M. C. Tuyn and H. I. Waterman)

[21] Tulleners, Tuyn and Waterman note that gasoline fractions can be used instead of alcohol or acetone in the preparation of the cooling medium.

In operation hydrogen chloride gas is admitted first to give the slight excess that favors rapid reaction, and then currents of the two gases (in about equimolecular proportions) are used. The reaction tube at the beginning of a run contains 40 g. of ethyl chloride and 10 g. of aluminum chloride. With a glass reaction vessel of 300 cu. cm. capacity, 180 liters of ethylene could be converted quantitatively into ethyl chloride within 1 hour. Operations on a semi-commercial scale could be carried out in an apparatus constructed of copper as this metal proved resistant to corrosion. On the other hand an iron reaction chamber, possibly because it was more readily corroded, seemed to exert a poisoning action on the catalyst.

With aluminum bromide as catalyst, ethylene and hydrogen bromide reacted smoothly and rapidly at —80°C., furnishing a good yield of ethyl bromide. In the absence of the metallic bromide this olefin does not react with liquid hydrogen bromide at room temperature although propene is rapidly converted under these conditions.[22]

An indirect method of producing alkyl halides, particularly ethyl chloride, has been described by Calcott and Daudt.[23] They continuously contact the absorption product of the olefin in sulphuric acid with an aqueous solution of a hydrogen halide in the liquid phase at temperatures above 100°C. Evolved vapors and also a portion of the liquid reaction product are continuously withdrawn and treated for the recovery of the alkyl halide.

Reaction with Organic Acids. The direct esterification of ethylene with organic carboxylic acids appears to be more difficult than in the case of the higher olefins. In a general way it is to be expected that this reaction, will be favored by the use of elevated pressures and moderate temperature, when operating in the gas phase.[24] Catalysts are usually essential for good yields and these include strong acids, such as sulphuric and phosphoric, as well as zinc chloride and other inorganic salts. In a process described by Graves,[25] an olefin (such as ethylene) and an organic acid (e.g., acetic) are continuously passed through concentrated sulphuric acid, saturated with the olefin. The temperature of the liquid is maintained above the boiling point of the desired ester. In the case of ethyl acetate 140°C. is sufficient. The effluent vapors are condensed and the ester separated from the condensate. Deterioration of sulphuric acid is retarded by circulation through a filter to remove suspended carbonaceous material.

According to Dreyfus,[26] ethyl esters of the lower aliphatic acids may be produced by contacting ethylene with the organic acid either in the liquid or gaseous phase. Temperatures of 350-550°C. are used and pressures of at least 5 atmospheres in the absence of strong mineral acids. For making ethyl acetate (and simultaneously some alcohol) a mixture of approximately 3 volumes of ethylene, 2 volumes of stearic acid and 1 volume of acetic acid is heated to 450°C. and repeatedly conducted over pumice. The last operation is effected under a pressure of 20 atmospheres. The products are afterwards separated by fractional distillation. As a modification, the vapors of petroleum hydrocarbons (boiling 200-350°C.) admixed with acetic acid are subjected to pyrolysis at 700°C. and atmospheric pressure in the absence of a catalyst. The resulting gases are cooled to

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[22] O. Maass and C. H. Wright, *J.A.C.S.*, 1921, 43, 1098; 1924, 46, 2664; *Chem. Abs.*, 1921, 15, 2369; 1924, 18, 2984.

[23] W. S. Calcott and H. W. Daudt, U. S. P. 2,016,072, Oct. 1, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 8004; *Brit. Chem. Abs.* B, 1936, 1140:

[24] See, for example, French P. 774,342, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 2176.

[25] G. D. Graves, U. S. P. 1,915,308, June 27, 1933, to E. I. du Pont de Nemours and Co.; *Chem. Abs.*, 1933, 27, 4243; *Brit. Chem. Abs.* B, 1934, 136.

[26] H. Dreyfus, U. S. P. 2,020,673, Nov. 12, 1935; *Chem. Abs.*, 1936, 30, 487.

400°C., compressed to 400 atmospheres pressure, and conducted over pumice impregnated with phosphoric acid.[27]

A method developed by Edlund and Evans[28] comprises reacting the olefin and organic acid in the presence of sulphuric acid and then allowing the reaction products to stratify as an ester-containing solvent phase and an acid layer. After separation, the ester is recovered by distillation. Unreacted olefin may serve as the solvent, or a saturated hydrocarbon (*e.g.*, butane or pentane) to serve in the latter capacity can be added to the reactants.

Another procedure involves hydrolyzing diethyl sulphate to ethyl alcohol, ethyl sulphuric acid, and sulphuric acid.[29] A calcium salt of a fatty acid, e.g., calcium acetate, is then incorporated, the quantity of salt being equivalent to about 80 per cent of the alkyl radical present, and the mixture distilled. In this manner a 94 per cent yield of ethyl acetate is said to be obtained from diethyl sulphate. In some instances acetic acid may be substituted for the calcium salt.[30] In such cases this process is applicable not only to the manufacture of ethyl acetate but also to the corresponding isopropyl and butyl esters.

The recovery of pure alkyl esters from the reaction products of calcium acetate and an acid liquor obtained by absorption of olefins in sulphuric acid, is described by Lebo and Beamer.[31] The mixture, after addition of some alcohol, is distilled and the condensed ester vapors are returned to the still: the operation is continued until water-formation practically ceases. When this occurs the ester vapors are subsequently conducted to a second stage where they are mixed with steam, and washed with water, and dried.

Young[32] reports the formation of organic cyanides by treatment of a solution of olefin in an inorganic acid (sulphuric or hydrohalogen) with sodium cyanide at 20°C.

PROPENE

The products of reaction between propene and sulphuric acid are isopropylsulphuric acid, $(CH_3)_2CHO—SO_3H$, and diisopropyl sulphate, $[(CH_3)_2CH]_2SO_4$. Both of these are intermediates in the commercial production of isopropanol. No *n*-propyl esters are formed in this reaction.[33]

In one commercial process, a gas containing propene is absorbed at normal pressure in 90 per cent sulphuric acid. An absorbent oil is added to increase the rate of solution of the gas. Operation is continued until the acid product contains a substantial proportion of diisopropyl sulphate. A product consisting mainly of the dialkyl sulphate is obtained when mixtures of propane and propene are agitated under pressure with about 85 per cent sulphuric acid or by contacting gaseous propene at 10-40°C. under pressures over 50 pounds per sq. in. with 65-85 per cent sulphuric acid, or, at 25°C. under 100 lbs. pressure with 80 per cent acid.[34] Under such conditions the formation of polymers is reported as almost entirely avoided. Absorption of gaseous propene in more concentrated sulphuric acid at low temperatures may also be employed.[35]

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[27] H. Dreyfus, British P. 402,060, 1933; *Brit. Chem. Abs.* B, 1934, 186; *Chem. Abs.*, 1934, **28**, 3079.

[28] K. R. Edlund and T. Evans, U. S. P. 2,006,734, July 2, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 5460. British P. 442,454, 1936, to Bataafsche Petroleum Maatschappij; *J. Inst. Pet. Tech.*, 1936, **22**, 168A; *Chem. Abs.*, 1936, **30**, 4511; *Brit. Chem. Abs.* B, 1936, 441. French P. 778,418, 1935; *Chem. Abs.*, 1935, **29**, 4374.

[29] W. S. Wilson, U. S. P. 1,979,515, Nov. 6, 1934, to Merrimac Chemical Co.; *Chem. Abs.*, 1935, **29**, 180; *Brit. Chem. Abs.* B, 1935, 938. British P. 440,363, 1934; *Brit. Chem. Abs.* B, 1936, 182; *Chem. Abs.*, 1936, **30**, 3835.

[30] W. S. Wilson, U. S. P. 1,979,516, Nov. 16, 1934, to Merrimac Chemical Co.; *Chem. Abs.*, 1935, **29**, 180; *Brit. Chem. Abs.* B, 1935, 938.

[31] R. B. Lebo and C. M. Beamer, U. S. P. 1,988,801, Jan. 22, 1935, to Standard Alcohol Co.; *Chem. Abs.*, 1935, **29**, 1833; *Brit. Chem. Abs.* B, 1936, 54.

[32] H. D. Young, U. S. P. 2,014,546, Sept. 17, 1935, to Van Schaack Bros. Chemical Works, Inc.; *Chem. Abs.*, 1935, **29**, 7345; *Brit. Chem. Abs.* B, 1936, 1032.

[33] B. T. Brooks, *J.A.C.S.*, 1934, **56**, 1998; *Chem. Abs.*, 1934, **28**, 6697; *Brit. Chem. Abs.* B, 1934, 1198. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

As in the case of ethylene, it seems likely that the initial reaction product between aqueous sulphuric acid and propene is a hydrated monoisopropyl ester, which subsequently reacts with more hydrocarbon to form water and the neutral di-ester, according to the following equations:

$$C_3H_6 + H_2SO_4(H_2O) \longrightarrow (CH_3)_2CHO{-}SO_3H{-}H_2O$$
$$C_3H_6 + (CH_3)_2CHO{-}SO_3H{-}H_2O \longrightarrow H_2O + (iso\text{-}C_3H_7{-}O)_2{-}SO_2$$

Evidence for the existence of the monoalkyl esters in a hydrated condition has already been presented in reference to ethylene[36]

Reaction with Halogen Acids. In the absence of specific catalysts, hydrogen chloride does not react with propene in the gaseous phase even at pressures as high as 105 atmospheres and temperatures up to 105°C. In the liquid phase, however, combination takes place fairly readily, the main product (isolated by Maass and his co-workers[37]) being isopropyl chloride, although some hexyl chloride was formed, particularly at lower temperatures. Later, Maass and Sutherland[38] investigated the velocity of reaction with rise in temperature when the reactants were maintained in the liquid state. Using a mixture of 2 moles of hydrogen chloride and 1 mole of propene (this mixture having a critical temperature of 70°C.) they found the velocity in liquid phase experiments to increase regularly with rising temperature up to about the critical temperature, above which it was uniformly zero.

In the presence of certain catalysts, however, hydrogen chloride readily combines with propene in the gas phase at atmospheric pressure. Brouwer and Wibaut[39] showed that, although this reaction was slow at room temperature in the presence of pure silica gel, its rate was markedly increased if the gel was impregnated with certain metallic chlorides. Examples of the latter are ferric chloride, bismuth chloride or zinc chloride which were efficient catalysts at room temperature but much less so at 80°C. At this higher temperature impregnation with mercuric, nickel, aluminum or calcium chloride was found effective. The reaction product consisted of about 97 per cent isopropyl chloride with a small proportion of higher-boiling products, probably hexyl chloride. No *n*-propyl chloride could be detected. The presence of oxygen in the reacting gases did not affect the course of the reaction. The peroxide effect (*q.v.*) was not observed when liquid hydrogen chloride combined with propene (to form only isopropyl chloride) in the presence of benzoyl peroxide.

A liquid mixture of propene and hydrogen bromide undergoes fairly rapid reaction even at room temperature. However, it has been shown by Ipatieff, Pines and Wackher[40] that no action occurs when pure propene gas is passed through a solution of hydrogen bromide in glacial acetic acid at 5°C. Certain organic compounds, such as hexane, cyclohexane, benzene and organic bromides, greatly accelerated the combination in acetic acid solution although polar compounds, such as

[34] B. T. Brooks and E. J. Cardarelli, U. S. P. 1,919,617, July 25, 1933, to Standard Alcohol Co.; *Brit. Chem. Abs.* B, 1934, 442; *Chem. Abs.*, 1933, 27, 4818.

[35] B. T. Brooks, *Ind. Eng. Chem.*, 1935, 27, 278.

[36] See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[37] O. Maass and C. Sivertz, *J.A.C.S.*, 1925, 47, 2883. H. S. Sutherland and O. Maass, *Trans. Roy. Soc. Canada*, 1926, 20 (3), 499; *Chem. Abs.*, 1927, 21, 2657; *Brit. Chem. Abs.* A, 1927, 441.

[38] H. S. Sutherland and O. Maass, *Can. J. Research*, 1931, 5, 48; *Brit. Chem. Abs.* A, 1931, 1239; *Chem. Abs.*, 1931, 25, 4771.

[39] L. G. Brouwer and J. P. Wibaut, *Rec. trav. chim.*, 1934, 53, 1001; *Chem. Abs.*, 1935, 29, 447; *J. Inst. Pet. Tech.*, 1935, 21, 47A; *Brit. Chem. Abs.* A, 1934, 1314.

[40] V. N. Ipatieff, H. Pines and R. C. Wackher, *J.A.C.S.*, 1934, 56, 2398; *Chem. Abs.*, 1935, 29, 988; *Brit. Chem. Abs.* A, 1935, 62; *J. Inst. Pet. Tech.*, 1935, 21, 14A.

water, alcohol and acetic acid, had no promoting effect. A rapid reaction was also observed when an equimolecular gaseous mixture of propene and hydrogen bromide was conducted through hexane. Ipatieff and his collaborators concluded that union between olefins and hydrogen bromide in the liquid phase is autocatalytic since the bromides formed during the reaction exert a definite catalytic influence. According to Sorokin, Belikova and Bogdanova,[41] the product of the action of propene on hydrogen bromide in glacial acetic acid solution is isopropyl bromide admixed with some *n*-propyl bromide.

In the method proposed by Strange and Kane,[42] propene and hydrogen chloride (or bromide) are contacted in the gaseous phase at a temperature below the normal boiling point of the resulting ester, e.g., at 80-120°C., with a solid porous adsorbent having a large surface area. Examples of such are silica gel or hydrous alumina mixed with iron turnings. The ester formed is periodically recovered from the catalyst mass by distillation under reduced pressure. Other adsorbent catalysts used by Strange and Kane[43] for this reaction include alumina gel prepared by co-precipitation of sodium aluminate and aluminum chloride in water, followed by drying at 150°C. for 2 hours and then at 250-300°C. for 2 hours more. Ferric chloride, vanadium or cerium salts may replace aluminum chloride, and alumina may be substituted by aluminum silicates or tin tungstates. The use of dehydrated alumina is described by Gayer.[44]

Lazier[45] made alkyl fluorides, such as propyl fluoride, by a vapor-phase combination of an olefin with hydrogen fluoride at elevated pressures and high temperatures. The catalysts employed were fluorides of multivalent elements such as manganese, cobalt, iron, aluminum or zinc. Thus, propyl fluoride is prepared by treatment of propene with gaseous hydrogen fluoride at 50 atmospheres and 250°C. with a contact agent consisting of activated charcoal impregnated with zinc fluoride. By carrying out the reaction in an inert solvent, such as dichloromethane or carbon tetrachloride, hydrogen fluoride may be added to unsaturated compounds having no triple linkings.[46] For example, products that may serve as insecticides or as textile auxiliaries are obtained by combining hydrogen fluoride with oleic or undecenoic acid, or with an olefin having at least 10 carbon atoms; *e.g.*, dodecene, $C_{12}H_{24}$.

Reaction with Organic Acids. Direct union of propene with various organic carboxylic acids appears to take place fairly readily in the liquid phase in the presence of certain catalysts. Sulphuric acid was used by Coleman[47] for direct esterification of olefins with anhydrous saturated carboxylic acids under superatmospheric pressures. Such a treatment of propene with glacial acetic acid assisted by sulphuric at about 125°C. produced isopropyl acetate. Metallic salts of strong acids (e.g., zinc chloride) were employed by Brezinski and Frolich[48] for esterification of olefins at 100-300°C. under pressures above 250 lb. per sq. in. Reaction may be carried out in an autoclave lined with aluminum or a non-corro-

[41] V. Sorokin, A. Belikova and O. Bogdanova, *J. Rubber Ind. Russia*, 1931, 5 (4-5), 26; *Brit. Chem. Abs.* A, 1934, 313; *Chem. Abs.*, 1933, 27, 5680.

[42] E. H. Strange and T. Kane, British P. 414,766, 1933; *Chem. Abs.*, 1935, **29**, 478; *Brit. Chem. Abs.* B, 1934, 920. French P. 769,103, 1934; *Chem. Abs.*, 1935, **29**, 478.

[43] E. H. Strange and T. Kane, British P. 435,858, 1935; French P. 787,340, 1935; *Chem. Abs.*, 1936, **30**, 1392; *Brit. Chem. Abs.* B, 1935, 1129.

[44] F. H. Gayer, U. S. P. 2,033,374, Mar. 10, 1936, to General Motors Corp.; *Chem. Abs.*, 1936, **30**, 2987.

[45] W. A. Lazier, British P. 406,284, 1932, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1934, 393; *Chem. Abs.*, 1934, **28**, 4744. U. S. P. 1,996,115, April 2, 1935; *Chem. Abs.*, 1935, **29**, 3352.

[46] British P. 453,830, 1935, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1936, 1192.

[47] G. H. Coleman, U. S. P. 2,021,851, Nov. 19, 1935, to Dow Chemical Co.; *Chem. Abs.*, 1936, **30**, 485; *Brit. Chem. Abs.* B, 1936, 1194. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[48] L. P. Brezinski and P. K. Frolich, U. S. P. 1,951,747, Mar. 20, 1934, Frolich to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1935, 138; *Chem. Abs.*, 1934, **28**, 3417.

sive alloy steel. At 150°C. under pressure approximately equimolecular proportions of propene and anhydrous acetic acid (containing a small proportion of acetic anhydride) and zinc chloride gave a 12.5 per cent yield of propyl acetate.

Boron fluoride has been shown by Dorris, Sowa and Nieuwland[49] to be an excellent catalyst for the liquid phase esterification of olefins under such mild conditions as 70°C. and pressures of about 25 cm. of mercury above 1 atmosphere. The isopropyl esters of acetic, monochloroacetic, dichloroacetic, trichloroacetic and benzoic acids were obtained in yields of 7, 34.2, 39.5, 48.4 and 88 per cent, respectively, by reacting propene with acids under conditions just given. Combination of propene with salicylic acid in the presence of boron trifluoride yields mainly 2-hydroxy-3-isopropylbenzoic acid and also the isopropyl ester. At the same time some isopropyl-2-hydroxy-3,5-diisopropylbenzoate is also produced. This suggests that isopropyl salicylate is first formed but undergoes further rearrangement and reaction with propene.[50]

Vapor-phase combination of olefins, such as propene, with aliphatic saturated monocarboxylic acids is effected by Strange and Kane[51] with the aid of metal salts of a strong mineral acid (such as the chlorides, bromides, phosphates or sulphates of zinc, aluminum, mercury, copper, cadmium, bismuth or antimony), or of a non-volatile strong mineral acid (sulphuric or phosphoric) or acidic derivative of such acids, e.g., sodium acid sulphate or benzene sulphonic acid. For example, 15 to 20 per cent yields of isopropyl acetate are secured by conducting approximately equal parts of propene and acetic acid vapor, at 110°C. and atmospheric pressure over a catalyst at the rate of 2 g. per cc. of catalyst per minute. The latter was prepared from 500 parts of adsorbent carbon and 50 parts of 75 per cent phosphoric acid, and dried at 150-250°C.[52]

BUTENES AND HIGHER ALIPHATIC OLEFINS

The higher olefins may be classified according to their behavior with sulphuric acid into two main groups, namely:

(a) Tertiary, or isoolefins, such as isobutene, trimethylethylene and 2-methylbutene-1, which react vigorously with relatively dilute (about 60 per cent) sulphuric acid and exhibit a marked tendency to polymerize with more concentrated acids;

(b) Secondary olefins, such as butene-1, butene-2, pentene-1, pentene-2, and hexene-2, which yield esters of secondary alcohols on sulphation with moderately concentrated sulphuric acid.

Isoolefins. The isoolefins, exemplified by isobutene, yield tertiary alcohols on absorption in sulphuric acid of 50-70 per cent concentration and subsequent hydrolysis of the alkyl sulphuric esters. So far as can be ascertained the corresponding di-esters have not been prepared since considerable polymerization occurs under conditions favoring their formation (i.e., use of more concentrated acids). This condensation may be prevented by the presence of metal cyanides or complex cyanides, or soluble platinum, copper, iron, cobalt, nickel or silver salts.[53] For changing isobutene into *ter.*-butyl sulphuric acid, use of acid concentrations of

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[49] T. B. Dorris, F. J. Sowa and J. A. Nieuwland, *J.A.C.S.*, 1934, 56, 2689; *Chem. Abs.*, 1935, 29, 724; *Brit. Chem. Abs.* A, 1935, 195.

[50] W. J. Croxall, F. J. Sowa and J. A. Nieuwland, *J.A.C.S.*, 1934, 56, 2054; *Chem. Abs.*, 1935, 29, 724; *Brit. Chem. Abs.* A, 1935, 1358.

[51] E. H. Strange and T. Kane, British P. 398.527, 1933; *Chem. Abs.*, 1934, 28, 1356; *Brit. Chem. Abs.* B, 1935, 1129. T. Kane, U. S. P. 2,014,850, Sept. 17, 1935, to E. H. Strange; *Chem. Abs.*, 1935, 29, 7343.

[52] Reaction of propene with sulphuric acid and its application in the commercial production of isopropanol are discussed in Chapter 14.

[53] Dutch P. 31,611, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, 28, 2368.

55-65 per cent at 10-35°C.[54] or 65 per cent at 10-15°C.[55] is advocated. Under these conditions the isobutene is selectively absorbed and any accompanying straight-chain butenes are recovered unchanged.

Secondary Olefins. For conversion of secondary olefins, such as the *n*-butenes, into their sulphuric acid esters, acid concentrations of 70-85 per cent at temperatures below 30°C. have been usually recommended. Under moderate pressures the hydrocarbon can be contacted in liquid form with the sulphuric acid. In this way butene-1 and butene-2 give esters of butanol-2 but pentene-1 yields esters of pentanol-2 exclusively. On sulphation of pentene-2 a mixture of esters derived from pentanol-2 (65 per cent) and pentanol-3 (35 per cent) is obtained.

Sulphation of isopropylethylene might be expected to yield esters of 3-methylbutanol-2. Actually, however, the initial product is the sulphuric ester of *ter.*-amyl alcohol, which, in the presence of acid concentrations necessary to react with this type of olefin, undergoes rapid polymerization.[56]

Mainly dialkyl esters derived from secondary alcohols having 4 or more carbon atoms are obtained by treating 90-100 per cent sulphuric acid with an excess of the corresponding olefin. The latter should be previously freed from tertiary olefins by treatment with 65-70 per cent sulphuric acid. Also reaction temperatures and pressures should be sufficiently low to maintain the olefin in liquid form.[57] Dibutyl sulphate is readily prepared in this way from the *n*-butenes.[58] Dialkyl sulphates of this type, formed during the sulphation of olefins for the production of the corresponding alcohols, separate from the acid liquor as an immiscible liquid phase on dilution with water.[59] They can be reconverted into the alkylsulphuric ester by heating with a 60-85 per cent aqueous solution of sulphuric acid.[60] Lacy[61] reports the production of dialkyl esters by absorption of ethylene homologues in sulphuric acid of about 75 per cent concentration followed by the addition of sufficient primary alcohol, such as ethanol, to satisfy the reactivity of the remaining sulphuric acid.

The purification of dialkyl sulphates by a process which includes their final distillation in the presence of less than 10 per cent sulphuric acid has been disclosed by Cox and Carruthers.[62] According to Brooks,[63] *sec.*-diamyl sulphate, a substance not hitherto known, can be prepared in 70-75 per cent yields by treating 90 per cent sulphuric acid at 15-20°C. with an excess of pentene-2. Dilution with water effects separation of the neutral ester and dissolved pentene-2.

Bertsch has made alkyl esters of persulphuric acid by reaction of the acid on high molecular weight olefins, such as hexadecene.[64]

Lee[65] has described the production of alkyl thiocyanates by treating the sulphuric acid ester of a secondary or tertiary alcohol with an alkali sulphocyanide.

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[54] G. A. Perkins and J. A. Davies, Canadian P. 350,409, 1935, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, **29**, 5127.

[55] B. T. Brooks, *Ind. Eng. Chem.*, 1935, **27**, 278; *Chem. Abs.*, 1935, **29**, 2700; *Brit. Chem. Abs.* B, 1935, 536.

[56] B. T. Brooks, *Ind. Eng. Chem.*, 1935, **27**, 287; *Chem. Abs.*, 1935, **29**, 2700; *Brit. Chem. Abs.* B, 1935, 536.

[57] German P. 577,947, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 489.

[58] W. Engs and R. Z. Moravec, U. S. P. 1,912,695, June 6, 1933, to Shell Development Co.; *Chem. Abs.*, 1933, **27**, 4240; *Brit. Chem. Abs.* B, 1934, 186.

[59] W. Engs and R. Moravec, U. S. P. 1,967,399, July 24, 1934, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 5832; *Brit. Chem. Abs.* B, 1935, 618.

[60] W. Engs and R. Moravec, U. S. P. 1,915,820, June 27, 1933, to Shell Development Co.; *Brit. Chem. Abs.* B, 1934, 136; *Chem. Abs.*, 1933, **27**, 4540.

[61] K. B. Lacy, U. S. P. 2,009,062, July 23, 1935, to Van Schaack Bros.; *Chem. Abs.*, 1935, **29**, 5855.

[62] H. L. Cox and T. F. Carruthers, U. S. P. 2,033,910, March 17, 1936, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1936, **30**, 2991.

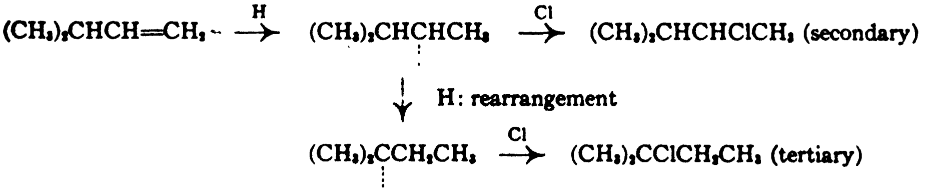
[63] B. T. Brooks, *Ind. Eng. Chem.*, 1935, **27**, 287; *Chem. Abs.*, 1935, **29**, 2700; *Brit. Chem. Abs.* B, 1935, 536.

[64] H. Bertsch, German P. 589,778, to Böhme A.-G.; *Chem. Abs.*, 1934, **28**, 2364.

[65] W. M. Lee, U. S. P. 1,992,533, Feb. 26, 1935; *Brit. Chem. Abs.* B, 1936, 138; *Chem. Abs.*, 1935, **29**, 2549.

For example, amylene is absorbed in 60 per cent sulphuric acid. To the resulting acid liquor, at 0°C., is added sodium thiocyanate. The product has a boiling range of 165-170°C.

Reactions of Tertiary Olefins. The tertiary olefins combine much more readily with hydrogen halides than do the isomeric secondary olefins. Leendertse, Tulleners and Waterman[66] found that both trimethylethylene and asymmetric methylethylethylene (2-methylbutene-1) combine readily at —80°C. with hydrogen chloride in the absence of catalysts. Under these conditions pentene-1 and pentene-2 react much more slowly and isopropylethylene practically not at all. Without catalysts at —80°C. the same reaction product, namely, *ter.*-amyl chloride or 2-chloro-2-methylbutane, was obtained from both of the branched chain pentenes while pentene-1 furnished a monochloropentane the structure of which was not determined. The union of these pentenes with hydrogen chloride at —80°C. was greatly accelerated by aluminum chloride in the presence of which pentene-2 yielded about 40 per cent of chloropentanes (boiling at 95-97°C.) and 60 per cent of monochlorides derived from the trimer, $(C_5H_{10})_3$. Under similar treatment, trimethylethylene and 2-methylbutene-1 gave a mixture of 2-chloro-2-methylbutane and monochlorides derived from the trimers of these olefins. The reaction of hydrogen chloride with isopropylethylene at —80°C. in the presence of aluminum chloride produced much 2-methyl-3-chlorobutane, together with a mixture of monochloro compounds formed by addition of hydrogen chloride to the olefins obtained by polymerization. On the other hand, Whitmore and Johnston[67] have found that the addition of hydrogen chloride to isopropylethylene in the dark at room temperature gives 88 per cent of a mixture of about equal amounts of tertiary and secondary amyl chlorides. The secondary chloride, recovered from the mixture after hydrolysis of the tertiary ester, boiled at 91.9°C. under 736 mm. and was stable when heated for 24 hours at 100°C. It did not react with water at room temperature. This addition reaction, according to Whitmore and Johnston, may be represented as



$$\begin{array}{lcl}
(CH_3)_2CHCH{=}CH_2 \xrightarrow{H} (CH_3)_2CH\dot{C}HCH_3 & \xrightarrow{Cl} & (CH_3)_2CHCHClCH_3 \text{ (secondary)} \\
\quad\quad\quad\quad \Big\downarrow \text{H: rearrangement} & & \\
(CH_3)_2\dot{C}CH_2CH_3 & \xrightarrow{Cl} & (CH_3)_2CClCH_2CH_3 \text{ (tertiary)}
\end{array}$$

The formation of a tertiary ester from isopropylethylene and hydrogen chloride is therefore the result of an intramolecular rearrangement similar to that occurring during the sulphation of this olefin.

From the mixture of amylenes and diolefins present in the fraction of vapor-phase cracked gasoline boiling at 30-42°C., the tertiary olefins, as well as the diolefins, are removed almost quantitatively by treatment with 37 per cent aqueous hydrochloric acid. Moor and Katzman[68] investigated this reaction and obtained their best results by using 2 moles of hydrochloric acid per unit of hydrocarbon fraction at 0-20°C. Above 20°C., polymerization is increased and reaction is much slower at —10°C. This treatment converted the tertiary amylenes into *ter.*-amyl chloride and largely polymerized the diolefins present, so that the residual unchanged hydrocarbons consisted mainly of secondary olefins. Moor and Katzman effect combination of the secondary amylenes (remaining after treatment with the aqueous acid) with hydrogen chloride in the gas phase at 115-120°C. using bismuth chloride on glass wool as a catalyst. Under these conditions the yield of secondary chlorides was 90 per cent. This decreased to 50 per cent at 100°C. and 21 per cent at 170-180°C. The bismuth chloride catalyst was slowly poisoned due to the formation of polymerized chloro hydrocarbons. By a combination of these two Moor and Katzman procedures, i.e., treatment with aqueous acid followed by that with gaseous hydrogen chloride, the total yield of secondary and tertiary amyl chlorides was 74 per cent of the initial material, the theoretical yield on this basis being 82 per cent.

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[66] J. J. Leendertse, A. J. Tulleners and H. I. Waterman, *Rec. trav. chim.*, 1934, 53, 715; *Brit. Chem. Abs.* A, 1934, 864; *Chem. Abs.*, 1934, 28, 5398; *J. Inst. Pet. Tech.*, 1934, 20, 447A.

[67] F. C. Whitmore and F. Johnston, *J.A.C.S.*, 1933, 55, 5020; *Chem. Abs.*, 1934, 28, 738; *Brit. Chem. Abs.* A, 1934, 168.

[68] V. G. Moor and S. V. Katzman, *Materials on Cracking*, *Goskhimtekhizdat* (*Leningrad*), 1933, No. 1, 121; *Chem. Abs.*, 1935, 29, 2717; *Brit. Chem. Abs.* B, 1935, 1031.

Triisobutylene can be directly combined with hydrogen chloride at —78°C. in the absence of a catalyst.[69] The resulting chloride, however, is not very stable. This instability may be an explanation of the low, and sometimes even negative, bromine values observed for polymerized hydrocarbons.

Aromatic vinyl compounds, such as styrene, easily react in the liquid phase with hydrogen chloride in the presence of substances capable of forming readily dissociable addition compounds with the hydrogen halide.[70] Examples of such are dimethyl aniline and other amines, acetone and methyl alcohol. Under these conditions styrene may be converted into α-chloroethylbenzene, $C_6H_5CHClCH_3$, Water may serve as a catalyst also if it is present in an extremely finely divided state.[71]

Tuot[72] has examined the reaction products of a number of higher monolefins with hydrogen bromide at 0°C. and from these has isolated a number of monobromo compounds. These together with some of their physical properties are given in Table 68. The bromides were readily hydrolyzed to the corresponding alcohols whose boiling points were 40 to 50°C. higher than those of the present olefins. This investigator also points out that the olefins suspended in dilute sulphuric acid are converted into non-distillable bromides by a mixture of potassium bromide and bromate.

TABLE 68.—*Physical Properties of Some Monobromides Derived from Octenes, Nonenes Decenes and Undecenes*

Compound	Boiling Point, °C.	d_{20}	20 D	Molecular Refraction	Surface Tension (Dynes/cm.) at 20°C.
2-Bromo-3-methylheptane	69° (12 mm.)	1.1235	1.4675	46.84	27.96
4-Bromo-2,4-dimethylhexane	67° (15 mm.)	1.1179	1.4554	46.88	27.54
2-Bromo-2,5-dimethylhexane	64° (15 mm.)	1.1044	1.4498	46.94	26.29
4-Bromo-2,4-dimethylheptane	80° (15 mm.)	1.0886	1.4558	51.62	27.27
5-Bromo-2,5-dimethylheptane	83° (16 mm.)	1.0909	1.4553	51.51	27.35
2-Bromo-2,3,5-trimethylhexane	79° (15 mm.)	1.1000	1.4594	51.49	28.48
4-Bromo-2,4-dimethyloctane	93° (14 mm.)	1.0759	1.4582	56.20	28.32
4-Bromo-2,4,6-trimethylheptane	83° (13 mm.)	1.0716	1.4568	56.10	27.80
4-Bromo-2,4,7-trimethyloctane	98° (11 mm.)	1.0524	1.4573	60.85	27.68

Reactions with Organic Acids. Olefins, such as isobutene and trimethylethylene, which give tertiary alcohols on hydration, combine with organic acids much more readily than their less branched isomers. Good yields of tertiary alkyl acetates may be obtained by reacting the olefin with the organic acid at room temperature in the presence of a small proportion of sulphuric acid as catalyst. For example, in the production of *ter.*-amyl acetate from isoamylene and acetic acid (containing some acetic anhydride) only a small proportion of sulphuric acid is employed, thus reducing polymerization of the olefin to a minimum.[73] Combination of anhydrous formic acid with the pentenes and hexenes present in the light fractions of cracked benzine takes place slowly without catalysts.[74] However, concentrated sulphuric acid (in small proportions) greatly accelerated the reaction although it later caused some decomposition of the esters. Rapid ester formation without appreciable polymerization was attained by repeatedly recycling the hydrocarbon material through the carboxylic acid containing a limited quantity of sulphuric acid.

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[69] H. I. Waterman, J. J. Leendertse and A. J. de Kok, *Rec. trav. chim.*, 1935, 53, 1151; *J. Inst. Pet. Tech.*, 1935, 21, 161A; *Chem. Abs.*, 1935, 29, 2504; *Brit. Chem. Abs.* A, 1935, 192.

[70] British P. 410,526, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1934, 617; *Chem. Abs.*, 1934, 28, 6446.

[71] French P. 745,533, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4253.

[72] M. Tuot, *Compt. rend.*, 1935, 200, 1418; *Chem. Abs.*, 1935, 29, 5067; *Brit. Chem. Abs.* A, 1935, 844.

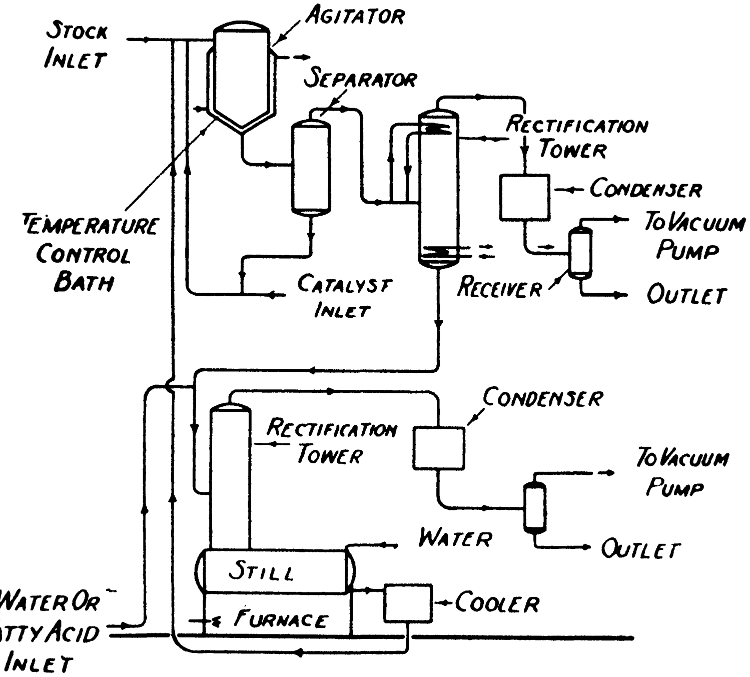

Fig. 98.—Flow Diagram of Method of Producing Alcohols and Esters from Olefins. (H. E. Buc)

The conversion was carried out as a continuous distillation process by allowing the olefin-bearing vapors to react in a side-tube with anhydrous formic acid in the presence of a small quantity of sulphuric acid. The esters were thus returned, immediately on formation, to the distilling flask. Polymerization of the olefins was in this way avoided and decomposition of the esters by the sulphuric acid minimized. Secondary and tertiary amyl and hexyl formates were produced almost quantitatively.

[73] W. M. Lee, U. S. P. 2,041,193, May 19, 1936, to Sharples Solvents Corp.; *Chem. Abs.*, 1936, 30, 4511.

[74] E. Sucharda and T. Mazonski, *Przemysl Chem.*, 1933, 17, 41; *Chem. Abs.*, 1933, 27, 5954; *Brit. Chem. Abs.* B, 1933, 497.

Direct union of some of the more reactive monolefins with strong organic acids, such as the chloroacetic acids, is known to occur readily in the absence of catalysts. Quantitative yields of *ter*-amyl chloroacetates were obtained by Nernst[75] at 30°C. although an equilibrium mixture of olefin and ester resulted at 100-150°C.

The influence of high pressures on reactions of the above type has been studied by Fawcett and Gibson.[76] At 30°C. from equimolecular proportions of trimethylethylene and trichloroacetic acid, they obtained (after 16 hours) yields of 18.6 per cent and 33.9 per cent of tertiary esters at 1 atmosphere and 3,000 atmospheres, respectively. From equimolecular proportions of bromethylethylene and acetic acid (without a catalyst) at 100°C., the ester yields in 16 hours were 1.1 per cent at atmospheric pressure and 6.6 per cent at 3,000 atmospheres. The corresponding figures for tests at 110°C. were 0.4 per cent and 4.5 per cent, respectively. A number of results by Fawcett and Gibson on the direct esterification of cyclohexene (2 moles) with trichloroacetic or dichloroacetic acid (1 mole) are summarized in Table 69.

TABLE 69.—*Non-Catalytic Esterification of Cyclohexene*

Acid Used	Temp., °C.	Time, Hrs.	Pressure, Ats.	Per Cent Acid Esterified
Trichloroacetic acid	30	16	1	Nil
" "	30	16	3,000	7.8
" "	60	40	1	37.9
" "	60	40	2,000	68.6
" "	60	40	3,000	74.7
" "	110	88	1	81.7
" "	110	88	3,000	92.3
Dichloroacetic acid	100	16	1	20.9
" "	100	16	3,000	54.1
" "	100	32	1	27.2
" "	100	32	3,000	60.3

A process for the manufacture of alcohols and esters from olefins has been described by Buc.[77] The hydrocarbon is first esterified with a relatively high-boiling halogen-substituted fatty acid, using an aqueous sulphuric acid catalyst. The product is separated from the acid catalyst and either hydrolyzed to the alcohol or converted into the ester of an unsubstituted fatty acid. For instance, more than 80 per cent of the olefin was converted into the monochloroacetic ester by agitating at 45°C. for 12 hours a mixture of 250 cc. of a hexene (obtained by dehydration of hexanol-2), 400 cc. of benzol (as diluent), 100 g. of monochloroacetic acid and 140 cc. of 80 per cent sulphuric acid. The acid catalyst was added slowly during the reaction period. The product can be separated from the acid catalyst and hydrolyzed to furnish hexyl alcohol.

EFFECT OF PRESSURE ON DIRECT ESTERIFICATION

In the direct esterification of the *n*-butenes and *n*-pentenes with organic acids, such as anhydrous acetic acid, it is necessary to heat the reaction mixture under pressure to obtain satisfactory yields. Brooks[78] reports that heating butene-2 under pressure to 115-120°C. with an excess ot glacial acetic acid containing 10 per cent sulphuric acid gives rise to secondary butyl acetate in yields up to 60 per cent of the theoretical. Before treating cracked hydrocarbon distillates for the production of *sec.*-butyl and amyl acetates by this procedure, Brooks[79] first selectively removes tertiary olefins and diolefins present.

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[75] W. Nernst. *Z. physik. Chem.*, 1893, 11, 353.

[76] E. W. Fawcett and R. O. Gibson, *J.C.S.*, **1934**, 386; *Chem. Abs.*, 1934, **28**, 4371; *Brit. Chem. Abs.* **A**, 1934, 603.

[77] **H. E. Buc, U. S. P. 1,939,384, Dec. 12, 1933, to Standard Oil Development Co.;** ***Chem. Abs.***, **1934, 28, 1356.**

[78] **B. T. Brooks,** ***Ind. Eng. Chem.***, **1935, 27, 278.**

One continuous esterification process comprises contacting an olefin-bearing material in the gaseous state with a countercurrent liquid stream of an anhydrous organic acid containing an esterifying catalyst. The operating temperature is kept above 50°C. but sufficiently low to permit removal of the ester in liquid form.[80] For example, *n*-butenes were treated with glacial acetic acid and sulphuric acid in the relative proportions (by volume) of 1.67, 1.0 and 0.25, respectively, for 3½ hours at 75°C. and under a pressure of 10 atmospheres. Butyl acetate was obtained in a 52 per cent yield (based on the acetic acid) and tar formation amounted to only 3 per cent.

If boron fluoride is utilized as the motivating agent, esters may be formed under normal temperature and pressure conditions.[81] Aliphatic, aromatic or cyclic acids may be esterified in this way, as well as acid mixtures obtained by oxidation of paraffin wax or liquid petroleum distillates. Gaseous or liquid olefins are adapted to the above combination, which may be represented by the following equation. R,R′ or R″ may be a hydrogen atom or a substituted group.

$$R'{-}CH{=}CH{-}R'' + RCOOH \longrightarrow R'{-}CHOOCR{-}CH_2{-}R''$$

One method of carrying out the process consists in preparing a solution of boron fluoride in the oxygenated organic compound and agitating the mixture by means of the olefin reactant. The secondary olefins[82] have been found especially susceptible for such direct esterifications. The unsaturation point may occur in a ring or cyclic compound, such as cyclohexene, as well as in straight chain aliphatic hydrocarbons. For example, 20 parts of pentene-2 were treated at room temperature with 10 parts of an acetic acid solution of boron fluoride. Hydrolysis of the product gave a yield of 10.5 parts of secondary amyl acetate. In another instance, 19 parts by weight of boron fluoride dissolved in 30 parts of acetic acid gave 36 parts by volume of solution. On reaction of the mixture with 100 parts by volume of pentene-2, the resultant liquor occupied a space of 124 parts. From the latter, 39 parts by volume of secondary amyl acetate were recovered. More dilute sulphuric acid is used for the higher olefins, such as amylene and hexene, and more concentrated acid for the lower olefins, such as propene. The pressure employed is somewhat lower than the vapor pressure of the particular hydrocarbon under treatment. The flow of material is regulated so that the time of contact is between 2 and 4 hours. Yields of almost 100 per cent ester based on the fatty acid may be obtained.

The ester is recovered from the reaction liquor by extraction, the solvent best adapted for the purpose being a low-boiling gasoline or pure hydrocarbon such as pentane or hexane. The sulphuric acid and solvent can then be returned, separately, to the system for re-use.

Isham[83] suggests that the olefin be reacted with a sulphonic acid, e.g., benzene or naphthalene sulphonic acid, and the resulting alkyl sulphonate then be converted into the ester by heating with a carboxylic acid. An alternate procedure comprises subjecting the olefin to the simultaneous action of sulphonic and carboxylic acids. Another method involves heating a dialkyl sulphate with calcium salts of organic acids in the presence of diluents. The latter may be either carbon tetrachloride[84] or a kerosene fraction containing substantially saturated hydrocarbons.[85]

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[79] B. T. Brooks, U. S. P. 1,894,662, Jan. 17, 1933, to Petroleum Chemical Corp.; *Brit. Chem. Abs.* B, 1933, 904; *Chem. Abs.*, 1933, 27, 2459.

[80] P. K. Frolich and P. L. Young, U. S. P. 1,877,291, Sept. 13, 1932, to Standard Oil Development Co.; *Chem. Abs.*, 1933, 27, 101. Also British P. 362,215, 1931; *Brit. Chem. Abs.* B, 1932, 332.

[81] H. G. Schneider, U. S. P. 2,065,540, Dec. 29, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1937, 31, 1036.

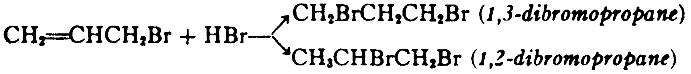
[82] In fact, the reaction may be used for the separation of secondary and tertiary olefins.

[83] R. M. Isham, U. S. P. 1,929,870, Oct. 10, 1933, to W. B. Pine; *Brit Chem. Abs.* B, 1934, 751; *Chem. Abs.*, 1934, 28, 173.

THE "PEROXIDE EFFECT" IN HYDROHALOGEN-OLEFIN ADDITION REACTIONS

In trying to establish the so-called relative electronegativity of various organic radicals, and in an extended study of the nature of the ethylene bond, some discrepancies between effects predicted by theory and those experimentally recorded led Kharasch and his co-workers to repeat the work on the combination of hydrogen bromide with allyl bromide and numerous other unsaturated compounds. Results obtained in these experiments seemed to indicate a definite effect of peroxides (or oxygen) on the direction of addition of halohydrogens to double-bonded hydrocarbons.

Allyl bromide reacts with hydrogen bromide in two different ways, namely,



$$CH_2{=}CHCH_2Br + HBr \begin{cases} \rightarrow CH_2BrCH_2CH_2Br \ (\textit{1,3-dibromopropane}) \\ \rightarrow CH_3CHBrCH_2Br \ (\textit{1,2-dibromopropane}) \end{cases}$$

An examination of this reaction, in the liquid phase and usually at room temperature, was carried out by Kharasch and Mayo.[86] They showed that although combination was very slow in the complete absence of oxygen or peroxides as well as in the presence of antioxidants,[87] the main product was 1,2-dibromopropane. With small amounts of oxygen or peroxides, a rapid reaction occurred with the almost exclusive formation of 1,3-dibromopropane. Factors such as presence of metallic salts as catalysts, use of various organic solvents and different temperatures or exposure to light all markedly affected the velocity of reaction but did not appear to exert any directive influence on it. The composition of the products was reported to depend entirely on the presence, or absence, of oxygen or peroxides. Similar conclusions were also reached in studies of the addition of hydrogen bromide to vinyl bromide[88] and to vinyl chloride.[89] In both cases, peroxides promoted formation of the 1,2-dihalogenated ethanes. On the other hand 100 per cent yields of the ethylidene (or 1,1-dihalogenated) compounds were obtained only in the absence of oxygen or peroxides as participants in the reaction.

Union of hydrogen bromide and allyl bromide in the presence of solvents and air was reported by Urushibara and Takebayashi[89a] to give 93 per cent of the 1,3-dibromo compound and 7 per cent of the 1,2-dibromo derivative. Some results obtained by these investigators with other catalysts are given in Table 69A. When reaction was effected in the absence of solvents, light and air, but employing reduced iron as the contact agent, yields of about 33 to 39 per cent of a mixture of dibromides were secured. Of the latter, 22 to 32 per cent was 1,2-dibromoallyl,

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[84] O. Spring, U. S. P. 1,924,575, Aug. 29, 1933, to Doherty Research Co.; *Chem. Abs.*, 1933, 27, 5338; *Brit. Chem. Abs.* B, 1934, 534.

[85] S. R. Merley and O. Spring, U. S. P. 1,924,615, Aug. 29, 1933, to Doherty Research Co.; *Chem. Abs.*, 1933, 27, 5338; *Brit. Chem. Abs.* B, 1934, 534.

[86] M. S. Kharasch and F. R. Mayo, *J.A.C.S.*, 1933, 55, 2468; *Chem. Abs.*, 1933, 27, 3444; *Brit. Chem. Abs.* A, 1933, 805.

[87] In this work the investigators were unable to observe any difference in results between the behavior of a reaction mixture freed beforehand from peroxides and run in vacuo, and that of one run in vacuo or in air in the presence of a good antioxidant. The use of the term "with antioxidant conditions" applies to a known absence of oxygen or peroxide (*per se* or in effect) from the active reagents, whether obtained by previous treatment or by addition to the reacting mixtures. Of the large number of antioxidants tested those mentioned in the cases described were found most applicable with the reagents under discussion.

[88] M. S. Kharasch, M. C. McNab and F. R. Mayo, *J.A.C.S.*, 1933, 55, 2521; *Chem. Abs.*, 1933, 27, 3444; *Brit. Chem. Abs.* A, 1933, 805.

[89] M. S. Kharasch and C. W. Hannum, *J.A.C.S.*, 1934, 56, 712; *Chem. Abs.*, 1934, 28, 2671; *Brit. Chem. Abs.* A, 1934, 508.

[89a] Y. Urushibara and M. Takebayashi, *Bull. Chem. Soc. Japan*, 1936, 11, 692; *Chem. Abs.*, 1937, 31, 1757.

TABLE 69A.—*Proportion of Dibromo Derivatives from Allyl Bromide and Hydrogen Bromide.*

Catalyst	1,3-Dibromo Derivative, %	1,2-Dibromo Derivative, %
None	7	93
Air	93	7
Sulphur	17	83
Nitric oxide	12	88
Reduced iron	71	29
Reduced nickel	68	32
Platinum black	12	88
Ferrous bromide (anhydrous)	7	93
Manganese sulphate (anhydrous)	7	93

and 68 to 78 per cent the 1,3-dibromide.[89b] Substitution of reduced nickel for iron likewise resulted in a preponderance of the 1,3-dibromide being formed. On the other hand nickel (exposed to air for 5 weeks) or cobalt (freshly reduced or not) favored development of the normal product, i.e., 1,2-dibromoallyl.

Kharasch, McNab and Mayo[90] also studied the directive influence of peroxides on the union of liquid propene and liquid hydrogen bromide. When benzoyl peroxide or ascaridole[91] was added, *n*-propyl bromide was secured almost quantitatively.[92] The addition of antioxidants, e.g., diphenylamine or *ter*.-butyl isocyanide, to the reactants gave rise to pure isopropyl bromide.[93] The latter compound was procured also when reaction was carried out in an atmosphere of air.

These results were confirmed by the work of Brouwer and Wibaut[94] who found that oxygen had no influence on the course of the vapor-phase combination of propene with hydrogen bromide. Using silica gel as catalyst, the addition reaction proceeded smoothly at room temperature, furnishing about 90 per cent of isopropyl bromide, a certain amount of a by-product (probably hexyl bromide) and only a little *n*-propyl bromide. Contact agents prepared by impregnating silica gel with the bromides of zinc, ferric iron, aluminum or bismuth were of less utility than the pure gel. The absence of substantial proportions of *n*-propyl bromide in the products of vapor-phase operations, even in the presence of oxygen, may be due to the non-formation of peroxides, as suggested by Kharasch. According to Brouwer and Wibaut, both isopropyl bromide and *n*-propyl bromide undergo partial isomerization when heated to 250-275°C. in sealed tubes. The equilibrium mixture obtained after 100 hours at 250°C. consisted of 70 per cent isopropyl bromide and 30 per cent *n*-propyl bromide. After 36 hours heating at 275°C. an equilibrium mixture contained 67 per cent iso- and 33 per cent *n*-propyl bromide.

It has been shown by Kharasch and Hannum[95] that at room temperature propene combines vigorously with hydrogen iodide in the liquid state to yield iso-

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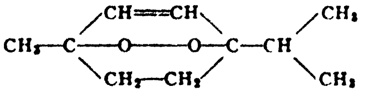
[89b] Y. Urushibara and M. Takebayashi, *Bull. Chem. Soc. Japan*, 1936, 11, 754; *Chem. Abs.*, 1937, 31, 1757.

[90] M. S. Kharasch, M. C. McNab and F. R. Mayo, *J.A.C.S.*, 1933, 55, 2531; *Chem. Abs.*, 1933, 27, 3444; *Brit. Chem. Abs.* A, 1933, 805.

[91] Ascaridole is a peroxide of menthene, as is shown by its structural formula:



It is the chief constituent of chenopodium or American wormseed oil in which it is found to the extent of 60-75 per cent. See T. T. Cocking and F. C. Hyams, *Analyst*, 1930, 55, 180; *Chem. Abs.*, 1930, 24, 2833.

[92] See also M. S. Kharasch, U. S. P. 2,058,466, Oct. 27, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, 31, 109.

[93] See also M. S. Kharasch, U. S. P. 2,058,465, Oct. 27, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, 31, 109.

[94] L. G. Brouwer and J. P. Wibaut, *Rec. trav. chim.*, 1934, 53, 1001; *Chem. Abs.*, 1935, 29, 447.

[95] M. S. Kharasch and C. Hannum, *J.A.C.S.*, 1934, 56, 1782; *Chem. Abs.*, 1934, 28, 6101; *Brit. Chem. Abs.* A, 1934, 1089; *J. Inst. Pet. Tech.*, 1934, 20, 522A.

propyl iodide exclusively. Peroxides did not change the course of the reaction and had no apparent influence on the time factor. It was suggested that the absence of the typical peroxide effect was due to rapid reduction and destruction of the peroxides by the halogen hydride. Similar observations were made in the case of butene-1 and neopentylethylene. With hydrogen iodide and allyl bromide, peroxides were found to exert a definite effect on reaction velocity and substantial conversions (68-81 per cent) of the olefin bromide into 1-bromo-2-iodopropane were obtainable only by their use.

Kharasch and his co-workers extended their study of the peroxide effect to the addition of hydrogen bromide to higher olefins. Thus, butene-1 furnished *sec.*-butyl bromide (2-bromobutane) quantitatively under antioxidant conditions. On the other hand, *n*-butyl bromide (1-bromobutane) was also formed in the presence of fairly large proportions of peroxides.[96] Since this reaction was not very sensitive to traces of peroxides, it was little influenced by external factors, such as solvents, temperature and light, which were found to affect only peroxide-catalyzed reactions of this type.

Union of hydrogen bromide and isobutene in the liquid phase has been investigated by Kharasch and Hinckley.[97] This reaction, which is rapid at room temperature, produces *ter*-butyl bromide exclusively under normal conditions, i.e., in the absence of peroxides. Other factors, such as temperature, light or solvents (glacial acetic acid and xylene) had little directive influence. However, with peroxides at least 80 per cent of the main reaction product was isobutyl bromide, $(CH_3)_2CHCH_2Br$. Since isobutene does not form peroxides readily, the latter bromide developed only in presence of added peroxides. Further work by Kharasch and Potts[98] indicated that under rigidly controlled antioxidant conditions, solvents (*e.g.*, pentane, carbon disulphide, ethyl bromide and nitrobenzene) have no directive influence on this addition although they markedly affect its velocity. In the presence of peroxides such as ascaridole, isobutyl bromide constituted 75-100 per cent of the total yield in the case of each solvent studied. Furthermore, Kharasch and Potts interpreted their results as showing that the apparent directive solvent effect noticed under other than antioxidant conditions was, in reality, an effect of the solvent upon the relative rates of the normal and the peroxide-catalyzed addition reactions.

By saturating pentene-1 or heptene-1, in organic solvents such as hexane, glacial acetic acid or carbon tetrachloride, with dry hydrogen bromide at atmospheric pressure and about 0°C., Sherrill, Mayer and Walter[99] found that the 1-bromo derivatives were formed exclusively. Prior to reaction the olefins gave no tests for peroxides. On the other hand, the addition products resulting from these olefins and aqueous hydrobromic acid (very slow reaction) at room temperatures during about two months, were exclusively the 2-bromo compounds. Accordingly, differences in the products by the two methods were attributed primarily to difference in solvents and not to presence of peroxides in the olefin. This conclusion has been contested by Kharasch, Hinckley and Gladstone.[100] They report that, under antioxidant conditions, pentene-2 combines with hydrogen bromide, either alone or in presence of glacial acetic acid, to yield at least 84 per cent

[96] M. S. Kharasch and J. A. Hinckley, Jr., *J.A.C.S.*, 1934, **56**, 1212; *Chem. Abs.*, 1934, **28**, 4372; *Brit. Chem. Abs.* **A**, 1934, 752.

[97] M. S. Kharasch and J. A. Hinckley, Jr., *J.A.C.S.*, 1934, **56**, 1243; *Chem. Abs.*, 1934, **28**, 4372; *Brit. Chem. Abs.* **A**, 1934, 752.

[98] M. S. Kharasch and W. M. Potts, *J.A.C.S.*, 1936, **58**, 57; *Brit. Chem. Abs.* **A**, 1936, 310; *Chem. Abs.*, 1936, **30**, 1734.

[99] M. L. Sherrill, K. E. Mayer and G. F. Walter, *J.A.C.S.*, 1934, **56**, 926; *Brit. Chem. Abs.* **A**, 1934, 630; *Chem. Abs.*, 1934, **28**, 3050.

[100] M. S. Kharasch, J. A. Hinckley, Jr., and M. M. Gladstone, *J.A.C.S.*, 1934, **56**, 1642; *Brit. Chem. Abs.* **A**, 1934, 989; *Chem. Abs.*, 1934, **28**, 5037; *J. Inst. Pet. Tech.*, 1934, **20**, 488A. M. S. Kharasch and M. C. McNab, *J.A.C.S.*, 1934, **56**, 1425; *Chem. Abs.*, 1934, **28**, 4371; *Brit. Chem. Abs.*

of 2-bromopentane. Also, in the presence of ascaridole and no solvents, 1-bromopentane is formed. According to Lauer and Stodola,[101] a mixture of 2- and 3-bromopentanes in about equal proportions is formed by interaction of pentene-2 with hydrogen bromide with or without glacial acetic acid as a solvent.

Brooks[102] compared the addition products of sulphuric acid and olefins of the type $RCH = CH_2$ with those obtained from the halogen acids and the same hydrocarbons. Treating pentene-1 with 85 per cent sulphuric acid differed from the addition of hydrogen bromide in yielding no primary derivatives for pentanol-2 was formed exclusively. The addition of hydrogen peroxide and finely powdered dibenzoyl peroxide to the reactants resulted in a product entirely free of any *n*-pentanol-1. The addition of sulphuric acid to pentene-2 gave a mixture of 65 per cent pentanol-2 and 35 per cent pentanol-3.

By passage of gaseous hydrogen bromide into 4,4-dimethylpentene-1 (at 0°C.), Whitmore and Homeyer[103] obtained only 1-bromo-4,4-dimethylpentene-1. They attributed this unusual mode of addition to the influence of the neopentyl group. However, Kharasch, Hannum and Gladstone[104] report that the 1-bromo-compound is formed only in the presence of peroxides (e.g., ascaridole). The "normal" addition compound, 2-bromo-4,4-dimethylpentane, is produced to a considerable extent in the presence of antioxidants (such as diphenylamine) in vacuo.

It is interesting to note that allyl acetic acid and hydrogen bromide, in hexane, formed only δ-bromovaleric acid ($CH_2BrCH_2CH_2CH_2COOH$) and the reaction was not reversed in the presence of hydrogen, diphenylamine or hydroquinone.[105] In the absence of a solvent either a freshly prepared sample of the unsaturated acid or one that gave a peroxide test yielded only γ-bromovaleric acid ($CH_3CHBrCH_2CH_2COOH$). However, when the diluent was not present, reversal of reaction (i.e., formation of δ-bromo acid) could be induced by the addition of dibenzoyl peroxide. Ashton and Smith[106] report that undecenoic acid either alone or in a solvent, in the absence of air, furnished only the 10-bromo acid. However, air or peroxides (for example, perbenzoic acid) gave rise to 11-bromoundecenoic acid. Ethyl undecenoate behaved similarly.[107] Isoundecenoic acid, however, always furnished a mixture of bromo acids (about 43 per cent of the 10-bromo compound) whether oxidants or antioxidants were present.[108] This probably indicated that only terminal double bonds were susceptible to the peroxide effect.

Treatment of styrene, dissolved in ethylbenzene, at 125°C. with hydrogen bromide is said to yield 63 per cent of α-bromoethylbenzene and 30 per cent of the β-bromo compounds.[109] If the temperature be reduced to 95°C. and benzoyl peroxide be added to the reaction mixture, then the yield of β-bromoethylbenzene is increased to 92 per cent.

A, 1934, 864. See also, M. L. Sherrill, *J.A.C.S.*, 1934, **56**, 1645; *Chem. Abs.*, 1934, **28**, 5037; *Brit. Chem. Abs.* A, 1934, 989; *J. Inst. Pet. Tech.*, 1934, 20, 488A.

[101] W. M. Lauer and F. H. Stodola, *J.A.C.S.*, 1934, 56, 1215; *Brit. Chem. Abs.* A, 1934, 753; *Chem. Abs.*, 1934, **28**, 4375; *J. Inst. Pet. Tech.*, 1934, 20, 407A.

[102] B. T. Brooks, *J.A.C.S.*, 1934, 56, 1998; *Brit. Chem. Abs.* A, 1934, 1198; *Chem. Abs.*, 1934, **28**, 6697.

[103] F. C. Whitmore and A. H. Homeyer, *J.A.C.S.*, 1933, 55, 4555; *J. Inst. Pet. Tech.*, 1934, **20**, 21A; *Chem. Abs.*, 1933, 27, 5716; *Brit. Chem. Abs.* A, 1933, 1271.

[104] M. S. Kharasch, C. Hannum and M. Gladstone, *J.A.C.S.*, 1934, 56, 244; *Brit. Chem. Abs.* A, 1934, 277; *Chem. Abs.*, 1934, 28, 1657.

[105] R. P. Linstead and H. N. Rydon, *Nature*, 1933, 132, 643; *Chem. Abs.*, 1934, 28, 464; *Brit. Chem. Abs.* A, 1933, 1275.

[106] R. Ashton and J. C. Smith, *J.C.S.*, 1934, 435; *Chem. Abs.*, 1934, **28**, 4379; *Brit. Chem. Abs.* A, 1934, 631.

[107] R. Ashton and J. C. Smith, *J.C.S.*, 1934, 1308; *Chem. Abs.*, 1935, **29**, 119; *Brit. Chem. Abs.* A, 1934, 1200.

[108] P. L. Harris and J. C. Smith, *J.C.S.*, 1935, 1108; *Brit. Chem. Abs.* A, 1935, 1223; *Chem. Abs.*, 1935, **29**, 7279. *Nature*, 1935, 135, 187; *Chem. Abs.*, 1935, **29**, 2504; *Brit. Chem. Abs.* A, 1935, 324.

[109] British P. 438,820, 1934, to Soc. des usines chimiques Rhone-Poulenc; *Brit. Chem. Abs.* B, 1936, 139; *Chem. Abs.*, 1936, **30**, 2993.

Chapter 13

Production of Ethyl Alcohol from Ethylene

The increasing use of ethyl alcohol as a motor fuel, as a solvent and as a chemical intermediate acts as an impetus for research on all phases of its production. Until the last few decades this important substance was manufactured on a large scale by the controlled fermentation of grains, molasses, potatoes and cellulose. However, over a long period of years efforts[1] have been made to synthesize ethanol from ethylene present in coke oven gas,[2] oil gas, coal gas or cracking gas. Other promising sources of materials which have been investigated are hydrocarbons[3] obtained by catalytic conversion of the carbon monoxide in illuminating gas or water gas, and that made available on oxidation of lean fuels or the gas from oxygen generators. According to information available, only two companies[4] have successfully commercialized the manufacture of alcohol from any of these last mentioned carbonaceous products.

Nevertheless, in spite of the prevailing low prices of the naturally occurring raw materials for fermentation, it was officially reported[5] that over 14,000,000 proof, or 7,000,000 wine, gallons of synthetic alcohol were produced from ethylene in the United States during the year ending June 30, 1932.

Since large quantities of olefins are available in the cracking gases of the petroleum industry many procedures have been investigated which have as their object the direct addition of water to the ethylene[5a] molecule according to the equation:

$$C_2H_4 + H_2O = C_2H_5OH$$

A review of recent researches on the utilization of the above reaction has already been summarized (Chapter 11). The present chapter is concerned only with the indirect hydration of ethylene by absorption in sulphuric acid and subsequent hydrolysis of the acid liquor. Commercially, this process for ethanol synthesis has given results of increasing promise. The reactions on which it is based are well-known and may be written as follows:

$$C_2H_4 + H_2SO_4 \longrightarrow C_2H_5SO_4H$$
$$C_2H_5SO_4H + H_2O \longrightarrow C_2H_5OH + H_2SO_4$$

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[1] For a discussion of these, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. See also, F. C. Whitmore, "Organic Chemistry," D. Van Nostrand Co., Inc., New York, 1937.

[2] For details of the earlier work by the Skinningrove Iron and Steel Works (England), see E. Bury and O. Ollander, *Cleveland Inst. Eng. Gas J.*, 1919, 718; *J.S.C.I.*, 1919, **38**, 470R; 1920, 94A; *Chem. Abs.*, 1920, **14**, 826. C. F. Tidman, *J.S.C.I.*, 1920, **39**, 86T, 103R; *Chem. Abs.*, 1921, **15**, 1391.

[3] Economic aspects of the synthetic alcohol industry are discussed by: N. Parravano, *Giorn. Chim. Ind. Appl.*, 1934, **16**, 425, *Brit. Chem. Abs.* B, 1934, 1093; *Chim. & ind.*, 1934 (*April Special No.*), 125; *Chem. Abs.*, 1934, **28**, 5803. B. T. Brooks, *Proc. World Petroleum Congr.*, 1933, **2**, 840; *Brit. Chem. Abs.* B, 1934, 742; *Refiner*, 1933, **12**, 353; *Chem. Abs.* 1934, **28**, 4871. Also, *Chem. Markets* (*N. Y.*), 1933, **33**, 331. A. Caille, *Bull. soc. ind. Rouen*, 1935, **63**, 133; *Chem. Abs.*, 1935, **29**, 6204.

[4] Compagnie de Béthune in France and the Carbide and Carbon Chemicals Corporation in the United States.

[5] J. M. Doran, *Rept. Comm. Ind. Alc.* (1931-2); *Ind. Eng. Chem.*, *News Ed.*, 1932, **10**, 308; *Chem. Trade J.*, 1933, **92**, 44.

[5a] For a discussion of other uses of ethylene, see *Chemistry and Industry*, 1937, 271.

EARLY WORK ON INDIRECT HYDRATION REACTIONS

Although the fact that ethylene can be absorbed in large quantities by concentrated sulphuric acid was undoubtedly first observed by Faraday,[6] it remained for Hennell,[7] working in the former's laboratory, to note the possibility of forming

> "either alcohol or ether, using olefiant gas as the hydrocarbon base: for I have shown in my last paper[8] that olefiant gas by combining with sulphuric acid forms sulphovinic acid, and the acid so produced forms ether or alcohol, according to circumstances which are under perfect command."

Berthelot has often been given full credit by many writers for this discovery. On the other hand, Meldola[9] (in 1895) gave Hennell full credit and ranked his discovery on a par with the synthesis of urea by Wöhler at about the same time (1828).

Herstein[10] has recently summarized the actual accomplishments of the two workers as follows:

"Hennell clearly indicated the possibility of preparing ethyl alcohol from ethylene by hydration via ethyl sulphuric acid and supported it by partial proof: the credit for complete proof and the extension of this reaction to olefins generally belongs to Berthelot."

There was no important industrial development of any method based on the reactions made known by Hennell and Berthelot until about a decade ago, and only in the last few years has there been any substantial progress in its commercial application.

CONTROLLING FACTORS IN ACID ABSORPTION PROCESS

From the economic viewpoint, the great disadvantage of the sulphuric acid absorption process is that relatively large amounts of diluted acid must be continually reconcentrated. This difficulty, of course, disappears if there is a market for the dilute product, for example, in the form of ammonium sulphate. In most cases, however, the problem must be handled in some other way. Hence the industrial success of the absorption process is entirely dependent upon the amount of alcohol which can be produced in one treatment from a given quantity of acid.

According to Brooks,[11] two chief factors have changed the commercial aspect of ethylene as a source of synthetic ethyl alcohol, viz.,

1. The development of simple methods for separating the higher olefins from the ethylene-containing gases;
2. Reduction in the acid requirement by application of elevated pressures for increasing the absorption of ethylene.

Production of ethyl alcohol from ethylene by this method involves essentially three separate stages of operation;

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[6] M. Faraday, *Phil. Trans. Roy. Soc.* (*London*) 1825, 488.

[7] H. Hennell, *ibid.*, 1828, 118, 365.

[8] H. Hennell, *ibid.*, 1826, 240.

[9] R. Meldola, Presidential Address before the British Association (1895); *Chem. News*, 72, 146. See also C. F. Tidman (*J.S.C.I.*, 1921, 40, 86T) for comment on the Hennell-Berthelot work.

[10] B. Herstein, *Chemistry and Industry*, 1935, 881; *Chem. Abs.*, 1936, 30, 336; *Brit. Chem. Abs.* A, 1935, 881.

[11] B. T. Brooks, *Ind. Eng. Chem.*, 1935, 27, 278; *Brit. Chem. Abs.* B, 1935, 536; *Chem. Abs.*, 1935, 29, 2700.

1. Absorption of ethylene in concentrated acid;
2. Dilution, hydrolysis and distillation of the ethyl alcohol formed;
3. Reconcentration of the dilute acid.

Discussion of the final stage of the process would be out of place in this book.

ABSORPTION OF ETHYLENE IN CONCENTRATED SULPHURIC ACID

The products of the absorption of ethylene in concentrated sulphuric acid consist of ethylsulphuric acid, $C_2H_5HSO_4$, and the neutral ester, diethyl sulphate, $(C_2H_5)_2SO_4$, as well as of small amounts of polymeric hydrocarbons.[12] The ease of absorption depends primarily on acid concentration, temperature, partial pressure of the ethylene; secondarily on the type catalysts used, if any, and on the apparatus employed in contacting the gas with the acid absorbent.

Concentration of Acid. As already pointed out, 98 per cent sulphuric acid appears to be most applicable for good yields of alcohol. Acid in 100 per cent concentration, besides being probably too costly, causes carbonization and renders temperature control difficult. Fuming sulphuric acid converts ethylene first into ethionic acid and then into carbyl sulphate.[13] The latter substance is formed exclusively by the action of gaseous sulphur trioxide on the olefin. Neither of these products is of value in the manufacture of ethyl alcohol.

The absorptive power of aqueous sulphuric acid towards ethylene rapidly diminishes with decreasing acid concentration even under high ethylene partial pressures. This is readily seen from Brooks' data which is discussed in Chapter 12.

Temperature. The absorption rate is increased by operating at temperatures up to about 75-80°C., above which side reactions such as decomposition, carbonization and formation of sulphur dioxide tend to become troublesome.

Pressure Effect. The use of high partial pressures of ethylene greatly increases both the speed of absorption and the quantity of the unsaturated hydrocarbon reacting with a given amount of sulphuric acid. In this connection, the results of experiments recorded by Brooks[14] are of interest. He points out that reduction in pressure from 500 to 200 lbs. per sq. in. is accompanied by a decrease in absorption from 1.25 to 0.6 moles of olefin per mole of acid.

By contacting ethylene with concentrated sulphuric acid (d 1.845) at 80°C. in a mixer rotated at 600-1000 r.p.m., Dalin and Gutuirya[15] obtained 1 kg. of ethyl alcohol per 3.2 kg. of sulphuric acid when working at atmospheric pressure. The acid consumption was reduced to 2.4 kg. per kg. of alcohol at 15 atmospheres pressure.

Strahler and Hachtel[16] investigated the absorption of ethylene in concentrated sulphuric acid at pressures up to 15 atmospheres. Their apparatus was an electrically-heated autoclave of V2A steel, fitted with a stirrer. The amount of sulphuric acid required to produce 1 kg. of ethanol was reduced from 5 kg. to 2 kg. by increasing the pressure from 1 up to 15 atmospheres. At 70°C., 15 atmospheres and a gas flow of 4 liters per hour per mole of acid, 400 g. of olefin had been absorbed per kg. of sulphuric acid (66°Bé.) after 24 hours. Of the original gas, 25 per cent was converted into diethyl sulphate, 3 to 5 per cent into polymers and the remainder into ethylsulphuric acid. Total absorption was not increased after the 24-hour period and was greatly reduced (under similar conditions) by the use of less concentrated acid.

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[12] *Cf.* Chapter 12. See also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[13] A. Michael and N. Weiner, *J.A.C.S.*, 1936, **58**, 294; *Chem. Abs.*, 1936, **30**, 2922; *Brit. Chem. Abs.* **A**, 1936, 453. For the reaction between olefins and sulphur dioxide, see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[14] B. T. Brooks, *Ind. Eng. Chem.*, 1935, **27**, 278. See also Chapter 12.

[15] M. A. Dalin and V. S. Gutuirya, *Azer. Neft. Khoz.*, 1934, No. 2, 90; *Chem. Abs.*, 1934, **28**, 7489; *Brit. Chem. Abs.* **B**, 1935, 395; *J. Inst. Pet. Tech.*, 1935, **21**, 418A.

[16] F. Strahler and F. Hachtel, *Brennstoff-Chem.*, 1934, **15**, 166; *Chem. Abs.*, 1934, **28**, 5805; *Brit. Chem. Abs.* **B**, 1934, 616; *J. Inst. Pet. Tech.*, 1934, **20**, 456A.

Nevertheless it has been proposed[17] to absorb ethylene, under pressures up to 250 atmospheres, in 60 to 75 per cent sulphuric acid at 90-150°C. The product is said to consist of a mixture of alcohol and ether, the proportion of the latter increasing with rising temperature of reaction. At 47 atmospheres pressure and 90°C., in 75 per cent acid, operation for 4 hours followed by hydrolysis and distillation furnished 119 g. of alcohol per kg. of sulphuric acid and practically no ether. At 140 atmospheres the yield was 166 g. of alcohol per kg. of acid. Brooks[18] proposes to synthesize ethyl alcohol from the mixture of ethylene and saturated hydrocarbons left after removal of higher olefins from cracking gases. The olefin-bearing residue, under pressures of 300-550 lbs. per sq. in., is contacted with 90-100 per cent sulphuric acid at 70-100°C. The resulting acid liquor is then hydrolyzed.

CATALYSTS FOR THE ABSORPTION REACTION

It has been recognized for some time that the absorption of ethylene in strong sulphuric acid is quickened by certain activators.[19] Actually the reaction is autocatalytic, being accelerated by ethylsulphuric acid itself.

Brooks and Schuler[20] report that the presence of about 10 per cent ether not only inhibits ether formation when the sulphuric ester is hydrolyzed to alcohol but actually promotes ester formation. In their experiments the acid was of 50-100 per cent concentration, and combination with ethylene was effected at 70-100°C. It was observed that less water was needed for the subsequent hydrolysis than was usually the case. On the other hand, Bailey and Calcutt[21] point out that when diethyl ether or nitrobenzene is dissolved in sulphuric acid not only is the surface tension of the latter lowered but also the solute molecules appear to be concentrated at the surface of the solution and thus decrease the rate of absorption of the olefin. In the case of the ether, each molecule concentrated in the surface layer seemed to prevent about 4 to 5 molecules of acid from reacting. The inhibitory action of nitrobenzene was attributed to its power of decomposing the ethylene-sulphuric acid complex, $C_2H_4 \cdot H_2SO_4$, which represented the first step in the absorption phenomenon. Both inhibitors were much less effective when the acid layer was agitated than when it was static.

Effect of Metallic Catalysts. Silver sulphate and cuprous chloride have been found by Strahler and Hachtel[22] to increase the initial rate of absorption when operating under 15 atmospheres pressure. However, the rate subsequently decreased and the total absorption was the same as that obtained in the absence of these metallic salts. In general, contact agents appear of doubtful value in large-scale operation. They tend to promote polymer formation, and rapid reaction can be attained by operating without them under pressure at about 80°C.

A systematic examination of a number of catalysts has been carried out by

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[17] W. P. Joshua and H. M. Stanley, U. S. P. 1,960,633, May 29, 1934, to Distillers Co. Ltd.; *Chem. Abs.*, 1934, **28**, 4430.

[18] B. T. Brooks, U. S. P. 1,919,618, July 25, 1933, to Standard Alcohol Co.; *Brit. Chem. Abs.* **B**, 1934, 442; *Chem. Abs.*, 1933, **27**, 4818.

[19] For a general review of the early application of catalysts, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[20] B. T. Brooks and R. Schuler, U. S. P. 2,006,157, June 25, 1935, to Standard Alcohol Co.; *Chem. Abs.*, 1935, **29**, 5457; *Brit. Chem. Abs.* **B**, 1936, 823.

[21] K. C. Bailey and W. E. Calcutt, *Sci. Proc. Roy. Dublin Soc.*, 1936, **21**, 309; *Chem. Abs.*, 1936, **30**, 6631; *Brit. Chem. Abs.* **A**, 1936, 1075.

[22] F. Strahler and F. Hachtel, *loc. cit.*

Gutuirya and Dalin.[23] They found that of a large variety of materials, only iron and silver were useful in the commercial production of alcohol. Some of the more active substances, such as cuprous chloride, seemed to lower the alcohol yield on prolonged contact. It was observed that satisfactory results could be obtained with iron at 65-70°C. This fact permits use of an iron contact apparatus, in the presence of which the metallic content of the acid increases by only about 0.3 to 0.4 per cent in 24 to 30 hours.

In this connection, Pigulevskii[24] reports that the absorption of propene in sulphuric acid, although autocatalytic, is markedly less accelerated by the presence of silver salts than is the case with similar treatment of ethylene or any of the butenes. According to Dalin and Gutuirya,[25] fused silica in small pieces is helpful when cracking gas is employed as the source of olefins.

Catalysts suggested by van Peski[26] include complex metallic cyano compounds. For the absorption of ethylene alone in about 96 per cent sulphuric acid, this investigator[27] mentions the use of compounds of copper, iron, cobalt or nickel (excluding complex organic compounds), as well as metals of the platinum group. The suggested catalysts included such substances as cuprous cyanide, cuprous oxide and cupric chloride as well as soluble complex compounds obtained by the action of carbon monoxide, or nitric oxide,[28] on the metal salts in acid solution, such as $Cu_2SO_4(CO)_x$ and $Cu_2SO_4(NO)_x$.

Organic Catalysts. For the manufacture of ethyl alcohol and ethyl ether from ethylene, Dreyfus[29] proposes to absorb this olefin in sulphuric or phosphoric acid containing water and at least 5 per cent of an ester of the inorganic acid. For example, ethylene is treated at 79°C. and 2 atmospheres pressure with 90 per cent sulphuric acid containing 5 per cent of glycol monosulphuric ester and 10 per cent of sulphoricinoleic acid. After hydrolysis the ethanol is recovered by distillation. The use of acids weaker than sulphuric, e.g., 40-80 per cent phosphoric or organic sulphonic acids, and high pressures (30-200 atmospheres) and temperatures (150-300°C.) has also been proposed by Dreyfus.[30] Catalysts may be present, such as silver, silver sulphate, cuprous oxide, as well as calcium, lead or ferrous sulphate.

TREATMENT OF GASES PRIOR TO ABSORPTION

Given a mixture of olefins, it is the usual practice to remove propene and its homologs by preferential absorption in more dilute sulphuric acid, prior to interaction of ethylene with more concentrated sulphuric acid. Dreyfus and Groombridge,[31] however, propose to extract propene from gas mixtures of this type by utilizing 80-90 per cent acid at 20-23°C. Ethylene in the residual gas is then treated with acid of lower concentration (75-85 per cent) at a higher temperature: in this case, 90 to 130°C.

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[23] V. S. Gutuirya and M. A. Dalin. *Azer. Neft. Khoz.*, 1935, No. 2, 89; *Chem. Abs.*, 1935, **29**, 7059; *Brit. Chem. Abs.* **B**, 1936, 918.

[24] V. V. Pigulevskii. *Trans. VI Mendeleev Congr. Theoret. Applied Chem.*, 1932, **2**, (1), 711; *Chem. Abs.*, 1936, **30**, 2734.

[25] M. A. Dalin and V. S. Gutuirya. *Azer. Neft. Khoz.*, 1933, No. 3, 66; *Brit. Chem. Abs.* **B**, 1933, 997; *Chem. Abs.*, 1933, **27**, 4211. See. V. Gerr, O. Pipik and F. Mezhebovskaya, *Refiner*, 1933, **12**, 96; *Chem. Abs.*, 1933, **27**, 2793. Also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[26] A. J. van Peski, U. S. P. 1,944,622, Jan. 23, 1934, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 2012. German P. 598,538, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 5831.

[27] A. J. van Peski, U. S. P. 1,979,018, Oct. 30, 1934, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 180.

[28] German P. 622,965, 1935, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 3442.

[29] H. Dreyfus, U. S. P. 2,015,105, Sept. 24, 1935; *Chem. Abs.*, 1935, **29**, 7342; *J. Inst. Pet. Tech.*, 1936, **22**, 54A. British P. 409,676, 1934; *Chem. Abs.*, 1934, **28**, 6156; *Brit. Chem. Abs.* **B**, 1934, 617; *J. Inst. Pet. Tech.*, 1934, **20**, 429A.

[30] H. Dreyfus, British P. 397,187, 1933; French P. 749,951, 1933; *Chem. Abs.*, 1934, **28**, 777; *Brit. Chem. Abs.* **B**, 1933, 904.

[31] H. Dreyfus and W. H. Groombridge, British P. 403,654, 1933, to British Celanese, Ltd.; *Chem. Abs.*, 1934, **28**, 3415; *J. Inst. Pet. Tech.*, 1935, **21**, 383A; *Brit. Chem. Abs.* **B**, 1934, 355.

The necessity of eliminating higher olefins from the ethylene fraction of cracking gas is pointed out by Gutuirya, Dalin and Shenderova.[31a] They find, when absorption of ethylene is carried out at atmospheric pressure, that an increase in the propene content (of the ethylene fraction) decreased the yield of ethanol by 29 per cent. Simultaneously the proportions of polymers and isopropyl alcohol formed rose to 8 and 35 per cent, respectively. At higher pressures (10 to 12 atmospheres) an increase in the propene content of the gases from 1 to 2 per cent resulted in a 22.5 per cent yield of polymers and 5.6 per cent of isopropanol.

Fussteig[32] reports tests made on removing ethylene from cracking gases. The use of sulphuric acid of increasing strength and a copper-silver-chloride catalyst was abandoned due to lack of contact between gas and acid as well as formation of mercaptans from the butadiene in the raw material. Selective adsorption by active carbon was adopted as most satisfactory. Dried gases from vapor-phase cracking had all olefins but ethylene extracted by activated charcoal at 40°C. Sulphuric acid of 66°Bé. concentration served to absorb the ethylene, from which alcohol could be obtained by the usual methods.

Contacting Apparatus

The rate of reaction between ethylene and sulphuric acid under any definite set of circumstances apparently depends markedly upon the type of apparatus employed. Conditions favoring the most intimate contact of gas with acid liquor give the best results. Countercurrent passage of gas and acid liquor in specially constructed towers is often employed, although mechanical agitation is likewise practiced. Dalin and Gutuirya[33] have reported efficient conversion in a mixer equipped with paddles and perforated discs and rotated at 600 r.p.m. Lower or higher speeds of the rotor resulted in lower absorption rates.

For ethylating sulphuric acid with a gas containing initially about 30 per cent ethylene and 70 per cent inert material, Stuart[34] employs a system of three towers in which the gas is scrubbed with the acid. The feed gas is passed in parallel through two of these towers containing acid of which the degree of ethylation increases (per mole of SO_3 present in any form) from 0 to 0.4 mole and from 0.9 to 1.3 mole, respectively. The exit gases from these columns are then passed through a third tower where ethylation of the acid increases from 0.4 to 0.9 mole of ethylene (per mole of SO_3). As soon as the upper limits of ethylation are attained, the path of the gas is rearranged after fresh acid has been substituted for the fully saturated liquor. This latter contains up to 1.25 mole of ethylene per mole of sulphur trioxide present as sulphuric acid, ethyl sulphuric acid and diethyl sulphate. The proportions of the final constituents may vary within wide limits. The process is intended for the selective extraction of one gas from a mixture of gases. The procedure described was planned to afford an exceptionally efficient scrubbing action just prior to the exit of the mixture from the system.

[31a] V. S. Gutuirya, M. A. Dalin and R. Shenderova, *Azer. Neft. Khoz.*, 1936, No. 5, 72; *Nat. Pet. News*, Apr. 21, 1937.

[32] R. Fussteig, *Chim. & ind.*, 1936, **35**, 1022; *Chem. Abs.*, 1936, **30**, 5934; *J. Inst. Pet. Tech.*, 1936. **22**, 295A.

[33] M. A. Dalin and V. S. Gutuirya, *Azer. Neft. Khoz.*, 1934, No. 2, 90; *Chem. Abs.*, 1934, **28**, 7487; *J. Inst. Pet. Tech.*, 1935, 21, 418A. See also *Gosud. Nauch. Tekh. Gorno-Geol. Neft. Izdat*, 1934, No. 3, 325; *Chem. Abs.*, 1935, **29**, 4564; *Brit. Chem. Abs.* **B**, 1936, 535.

[34] K. E. Stuart, U. S. P. 1.993.421, March 5, 1935, to Hooker Electrochemical Co.; *Chem. Abs.*, 1935, **29**, 2550; *Brit. Chem. Abs.* **B**, 1936, 53.

Kramer[35] describes an apparatus in which olefins of the type $R_2C = CHR$, dissolved in a mineral oil, are contacted in countercurrent with the absorbing acid (sulphuric) in a series of alternate agitating and settling chambers. Contiguous chambers only are connected. Hydrostatic heads of acid and olefin-bearing oil in the settling zones are in the same ratio as the amounts of these two liquid phases in the agitating zones. The treated material is removed from the apparatus at a settling compartment. Sulphation of olefins may also be effected, according to this same investigator,[36] in the presence of a circulating liquid medium of large heat capacity. Precooling below the maximum reaction temperature avoids exceeding the temperature at which the product desired is stable. The circulating fluid may be an inert liquid or one of the reactants, or an easily separable secondary reaction product.

HYDROLYSIS OF ETHYLATED SULPHURIC ACID LIQUORS

The alkyl hydrogen sulphates, although fairly stable in the presence of water at ordinary temperatures, are rapidly hydrolyzed on heating. The rate of hydrolysis is greatly accelerated by hydrogen ions[37] and for this reason takes place readily in dilute acid solution. In alkaline solution the monoalkyl sulphates (or, rather, their alkali salts) are only very slowly hydrolyzed, even on boiling. In moderately concentrated sulphuric acid solutions, an equilibrium is set up between alkylsulphuric acid, water, free sulphuric acid and alcohol, according to the equation,

$$ROSO_3H + H_2O \rightleftharpoons ROH + H_2SO_4$$

Hydrolysis of Ethylsulphuric Acid. In the case of ethylsulphuric acid, substantial proportions of ethyl alcohol are present in the equilibrium mixture even with relatively concentrated sulphuric acid. However, the recovery of ethanol by heating the mixture is not feasible because dehydration to ethylene and also to ether tends to occur. In fact, the degree of dilution with water necessary in the industrial production of alcohols is largely controlled by the necessity of suppressing such undesirable or analogous side reactions. These secondary combinations are in general more pronounced with the higher olefins than with ethylene. In the case of ethyl or isopropyl hydrogen sulphates, hydrolysis and distillation may be carried out in solutions of 35 per cent sulphuric acid without appreciable breaking down of the alcohol molecule. With the higher monoalkyl sulphates, olefin formation, usually accompanied by polymerization, is always a controlling factor.[38]

Hydrolysis of Dialkyl Sulphates. The dialkyl sulphates are also hydrolyzed in the presence of hot water and the reaction is accelerated by hydrogen ions. In moderately concentrated sulphuric acid solution an equilibrium is set up as follows:

$$(RO)_2SO_2 + H_2O \rightleftharpoons ROSO_3H + ROH$$

However, the hydrolysis of the dialkyl sulphates is complicated by ether formation even in fairly dilute acid solutions, which does not happen in the case of the monoalkyl sulphates. Thus, while ethyl alcohol may be distilled without appreciable ether production from a 40 per cent sulphuric acid solution, the addition of diethyl sulphate to such a mixture causes as much as 30 per cent of this ester to be converted into ether, probably thus:

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[35] G. A. Kramer, U. S. P. 1,953,618, April 3, 1934, to Shell Development Co.; *Brit. Chem. Abs.* **B**, 1935, 138; *Chem. Abs.*, 1934, **28**, 3740.

[36] G. A. Kramer, U. S. P. 1,967,410, July 24, 1934, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 5831; *Brit. Chem. Abs.* **B**, 1935, 531.

[37] W. A. Drushel and G. A. Linhart, *Amer. J. Sci.*, 1911, **32**, 51; *Chem. Abs.*, 1911, 5, 3365. See B. T. Brooks, *Ind. Eng. Chem.*, 1935, **27**, 278; *Chem. Abs.*, 1935, **29**, 2700; *Brit. Chem. Abs.* **B**, 1935, 536.

[38] B. T. Brooks, *Ind. Eng. Chem.*, 1935, **27**, 278; *Brit. Chem. Abs.* **B**, 1935, 536; *Chem. Abs.*, 1935, **29**, 2700.

$$(C_2H_5O)_2SO_2 + C_2H_5OH \longrightarrow (C_2H_5)_2O + C_2H_5O \cdot SO_3H$$

According to Brooks,[39] this reaction, discovered long since by Erlenmeyer,[40] is mainly, or wholly, responsible for the formation of ethyl ether in the customary method of preparation, viz., treatment of alcohol with sulphuric acid.

The formation of ethyl ether[41] in the hydrolysis of diethyl sulphate may be minimized by separating the ester from the acid reaction product, which may be hydrolyzed separately with water or dilute acid. An alternate method is to add the ester gradually to boiling water in which the alcohol concentration is kept low by continuous distillation.

For the hydrolysis of an acid liquor containing mainly ethylsulphuric acid and unchanged sulphuric acid, Dalin and Gutuirya[42] recommend dilution with 53 parts by weight of water for 47 parts of acid liquor, followed by distillation and rectification. The same investigators[43] have reported alcohol production by treatment of petroleum gases carrying 17-18 per cent ethylene. Absorption in a concentrated medium was carried out at 65-75°C. under 15-20 atmospheres pressure. The resulting liquor, after dilution with an equal weight of water, was heated to 160-170°C. in a tube still. The product collected was 92-94 per cent alcohol.

Groombridge and Peek[44] recover alcohol or ether from acid liquors by hydrolysis with an equal weight of water. The mixture passes down a copper column packed with pumice and indirectly heated to 125-130°C. at the base. Vapors of the product distil off from the top and the acid is said to be regenerated by the time it reaches the bottom of the tower. Stuart[45] recommends introducing the acid alkyl sulphate material in regulated proportions into a stream of water at intervals along the line of flow. The alcohol formed may be collected after distillation.

When ethylene has been absorbed in sulphuric acid and the mixture contains flocculent carbonaceous impurities, due to polymer formation, two methods of treatment are available:

1. The esters may be first hydrolyzed by dilution with not less than two volumes of water, and the dialkyl sulphate[46] extracted with a water-immiscible solvent, such as diethyl ether.

2. Dilution by not less than 4 volumes of ethyl alcohol or ether may precede filtration to remove precipitated impurities. The diethyl sulphate[47] is then separated after hydrolysis of the filtrate with water.

Another process[48] involves the use of 90-100 per cent sulphuric acid at 70-80°C. for the absorption of ethylene. Under these conditions, with 20 atmospheres pressure, a high percentage of diethyl sulphate is obtained. This ester may be separated by distillation above 130°C. at 20 mm. pressure. Hydrolysis with water and distillation produces ethyl alcohol. It is reported that no ether is formed in this procedure and that the dilute acid is free from carbon.

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[39] B. T. Brooks, *Ind. Eng. Chem.*, 1935, 27, 278; *Brit. Chem. Abs.* B, 1935, 536; *Chem. Abs.*, 1935, 29, 2700.

[40] E. Erlenmeyer, *Ann. Chem. Pharm.*, 1872, 162, 373; *J.C.S.*, 1872, 25, 605.

[41] See also B. T. Brooks and R. Schuler, *loc. cit.*

[42] M. A. Dalin and V. S. Gutuirya, *Gosud. Nauch. Tekh. Gorno-Geol. Neft. Izdat.*, 1934, No. 3, 325; *Chem. Abs.*, 1935, 29, 4564; *Brit. Chem. Abs.* B, 1936, 535.

[43] V. S. Gutuirya and M. A. Dalin, *Azer. Neft. Khoz.*, 1934, No. 5, 58; *Chem. Abs.*, 1935, 29, 5642; *Brit. Chem. Abs.* B, 1936, 484.

[44] W. H. Groombridge and R. J. Peek, British P. 428,792, 1933, to British Celanese, Ltd.; *Brit. Chem. Abs.* B, 1935, 664; *Chem. Abs.*, 1935, 29, 6901.

[45] K. E. Stuart, U. S. P. 2,013,453, Sept. 3, 1935, to Hooker Electrochemical Co.; *Chem. Abs.*, 1935, 29, 6901; *Brit. Chem. Abs.* B, 1936, 919.

[46] T. F. Carruthers, U. S. P. 1,949,366, Feb. 27, 1934, to Carbide & Carbon Chemicals Corp.; *Brit. Chem. Abs.* B, 1935, 13; *Chem. Abs.*, 1934, 28, 2731.

[47] H. L. Cox, U. S. P. 1,949,369, Feb. 27, 1934, to Carbide & Carbon Chemicals Corp.; *Brit. Chem. Abs.* B, 1935, 13; *Chem. Abs.*, 1934, 28, 2731.

[48] British P. 446,614, 1936, to Standard Alcohol Co.; *Brit. Chem. Abs.* B, 1936, 919; *Chem. Abs.*, 1936, 30, 6765.

Dreyfus[49] recovers ethyl alcohol from diluted and hydrolyzed acid liquor by either of two methods:

1. Use of certain selective solvents, such as chlorobenzene, hydrogenated naphthalene or tetrachloroethane; or
2. Azeotropic distillation in the presence of an entraining agent such as benzene, chloroform, trichloroethylene, *n*-hexane or cyclohexane.

Sargent[50] recommends that an alkyl sulphate mixture, derived from olefins of less than 4 carbon atoms and carrying a considerable proportion of dialkyl sulphate be mixed with not more than an equal weight of water. After the resultant emulsion has been agitated at 70-80°C. for 20 minutes to 1 hour, alcohol and ether may be recovered by distillation. If this is continued until the density of the distillate is 0.999, the concentration of the sulphuric acid in the still should be about 67-72 per cent.

Hydrolysis of Diethyl Sulphate. Graham[51] effects hydrolysis of diethyl sulphate liquor by regulating its addition to boiling water so that the alcohol distils out of the water continuously as rapidly as the sulphate liquor is added. A larger yield of alcohol is thought to be possible in this way than by the usual methods. An analogous procedure has been described by Scott, Bovier and Matthews.[52] Wilson[53] removes acid from the zone of reaction by hydrolyzing alkylated liquors in the presence of bauxite, or with water alone, followed by neutralization of the free acid with bauxite. Alcohols and aluminum sulphate are produced.

The effect of strong acids on the alkyl sulphates is emphasized by the following reactions reported by Kohler.[54] The acid used in his experiments was hydrogen chloride in the gaseous form.

$$C_2H_5SO_4K + HCl = KHSO_4 + C_2H_5Cl$$
$$(C_2H_5SO_4)_2Ba + 2HCl = BaSO_4 + H_2SO_4 + 2C_2H_5Cl$$

The potassium acid sulphate formation was reported as proceeding quantitatively at 145°C. The barium salt was completely decomposed at 65 to 80°C.

The effect of moisture on diethyl sulphate, with consequent damage to containers used for storage, has been investigated by Siebeneicher.[55]

TECHNICAL PROCEDURES

According to Sidersky,[56] one widely discussed commercial plant[57] for the production of synthetic alcohol separates an ethylene-rich fraction from coal gas by fractional liquefaction and distillation. The olefin is absorbed under high pressure by a liquor composed of sulphuric and ethylsulphuric acids. The product is then said to be hydrolyzed by blowing steam through the acid medium. The yield of alcohol is reported as 6.5-10.8 liters per ton of coal.

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[49] H. Dreyfus, British P. 410,816, 1934; *Chem. Abs.*, 1934, **28**, 6443; *Brit. Chem. Abs.* **B**, 1934, 665. French P. 761,776, 1934; *Chem. Abs.*, 1934, **28**, 4067.

[50] N. A. Sargent, British P. 427,223, 1935; *Chem. Abs.*, 1935, **29**, 6245; *Brit. Chem. Abs.* **B**, 1935, 619.

[51] R. N. Graham, Canadian P. 343,369, 1934, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1934, **28**, 6727.

[52] W. B. Scott, Z. S. Bovier and E. D. Matthews, U. S. P. 2,004,084, June 4, 1935, to Hooker Electrochemical Co.; *Chem. Abs.*, 1935, **29**, 4776.

[53] W. S. Wilson, U. S. P. 1,931,014, Oct. 17, 1933, to Merrimac Chemical Co.; *Chem. Abs.*, 1934, **28**, 173; *Brit. Chem. Abs.* **B**, 1934, 872.

[54] H. Kohler, *Ber.*, 1878, 11, 1929; *J.C.S.*, 1879, **36**, 137.

[55] K. Siebeneicher, *Angew. Chem.*, 1934, 47, 105; *Chem. Abs.*, 1934, **28**, 2908; *Brit. Chem. Abs.* **B**, 1934, 392. See also Chapter 12.

[56] D. Sidersky, *Bull. Assoc. Chim. Sucr. Dist.*, 1931, **48**, 163; *Chem. Zentr.*, 1931, **2**, 1630.

[57] Reference is here made to the plant of the Compagnie de Bethune. A sample of their product was found to contain 0.05 per cent acetaldehyde, 0.3 per cent acetone, and 3.7 per cent isopropanol. After repeated fractional distillations 1 per cent of the latter was still present. The tests were made by J. Stastny and V. Vilikovsky (*Vestnik Ceskoslov. Akad. Zemidilske*, 1934, 10, 526; *Chem. Abs.*, 1936, **30**, 3402) who report convenient analytical procedures for the determination of acetone and isopropyl alcohol.

A semi-commercial plant in Russia has also been described.[58] In one semi-technical unit, the ethylene-containing material (cracking gas) was freed from high olefins by passage over active carbon. From the latter, the higher olefins could be expelled periodically by the use of superheated steam.[59]

DEHYDRATION OF ETHYL ALCOHOL

Fractional distillation of aqueous ethyl alcohol in the absence of entraining agents is not sufficient to yield anhydrous alcohol. A constant boiling mixture with water is always obtained, the composition of this azeotrope depending on the pressure at which fractionation is carried out. Under normal conditions, the azeotropic mixture contains 95.57 per cent by weight of ethyl alcohol and 4.43 per cent of water; it boils at 78.15°C. For many industrial purposes alcohol containing not more than about 0.2 per cent of water is required. Several processes are available for preparing this so-called "absolute alcohol" by dehydration of the alcohol-water azeotrope that results from simple fractionation. The familiar use of quick lime for this purpose has been supplanted by the more economical method of azeotropic distillation for which benzene and similar entraining liquids are applicable.[60]

Several azeotropic distillation methods are in commercial use and a large proportion of the total absolute alcohol produced is obtained in this manner. A mixture of benzene and a gasoline fraction is employed as dehydrating agent at atmospheric pressure in the Guinot[61] process. In another plant of the same type[62] dehydration is effected azeotropically by means of benzene under a working pressure of 10 atmospheres. In a third azeotropic dehydration system, known as the Drawinol process,[62a] stabilized[63] trichloroethylene functions as the entraining agent.[64]

In azeotropic dehydration of ethyl alcohol, since vapors from the rectification stage are used for heating the dehydration stage, Renotte[65] proposes to concentrate the alcohol in the former stage to a point considerably below 96° Gay Lussac.[66] Under these conditions the heat required for dehydration corresponds to that supplied by the alcohol vapors from the rectifiers. An economy of fuel is possible by this method of operation.

[58] Developed by the Oil Institute of Baku. See. *Sotsialist Rekonstruksiya i Nauka*, 1935, No. 4, 168; *Chem. Abs.*, 1936, **30**, 1358.

[59] M. A. Dalin and V. S. Gutuirya, *Azer. Neft. Khoz.*, 1933, No. 8, 40; *Brit. Chem. Abs.* **B**, 1935, 395; *Chem. Abs.*, 1934, **28**, 7489.

[60] Reviews of various dehydrating processes are given by V. Siedler (*Petroleum Z.*, 1934, **30**, No. 36, 1; *J. Inst. Pet. Tech.*, 1934, **20**, 576A) and by R. Fritzweiler and K. R. Dietrich (*Proc. World Petr. Congr.*, 1933, **2**, 784; *J. Inst. Pet. Tech.*, 1934, **20**, 258A).

[61] Usines de Melle, France.

[62] Merck & Co.

[62a] Developed by the German Government Administration of Alcohol Monopoly.

[63] A. L. Pitman stabilizes trichloroethylene by the addition of very small amounts of hexylresorcinol (0.001 per cent) or triethylamine (0.0005 per cent): U. S. P. 1,910,962, May 23, 1933, to Westvaco Chlorine Products Inc., and 1,925,602, Sept. 5, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, **27**, 3951, 5445; *Brit. Chem. Abs.* **B**, 1934, 86, 617.

[64] E. Luhder, *Z. Spiritusind.*, 1934, **57**, 252; *Brit. Chem. Abs.* **B**, 1934, 1030; *Chem. Abs.*, 1935, **29**, 3453.

[65] J. Renotte, British P. 409,053, 1934; *Brit. Chem. Abs.* **B**, 1934, 552; *Chem. Abs.*, 1934, **28**, 5922; *J. Inst. Pet. Tech.*, 1934, **20**, 428A.

[66] According to Watt's Dictionary (1872), Gay Lussac's determinations of sp. gr. were made at 15°C. The 96° alcoholometer reading refers to 96 per cent alcohol by volume.

Absolute ethyl alcohol obtained commercially by azeotropic distillation is said[67] to have the following physical constants:

Density (25°C.)	0.78523
Boiling point	78.38°C.
Rate of change of b.p. with pressure..	0.034°C./mm.Hg.

Physical constants and analytical data on benzine, as used in Poland for dehydration of alcohol by azeotropic methods, have been made available by Sosnowski and Treszczanowicz.[68] Compositions and boiling points of the azeotropic, or benzine-alcohol, and of the heteroazeotropic or benzine-alcohol-water systems have been determined. The benzine consisted of 69 per cent heptane. In carrying out an azeotropic dehydration of ethyl alcohol, the boiling points of "heteroazeotrope" (64 vol. per cent benzine, 5 per cent water and 31 per cent alcohol) and "azeotrope" (52.6 per cent benzine and 47.4 per cent alcohol) were, on the average, 69.7°C. and 72.5°C., respectively.

It is to be noted that solid dehydrating agents appear to be coming into use again. In the Gyp process,[69] wet alcohol vapors are contacted in a countercurrent system with a stream of finely-divided anhydrous gypsum (dried at not less than 160-180°C.). The anhydrite is converted into a semi-hydrate and the alcohol produced is reported as about 99.8 per cent pure.[70] The used anhydrite is regenerated by air-drying at about 175°C. Steam consumption in this process is said to be only 40 kg. per hectoliter of alcohol. The process is carried out in a very small space and requires no columns and no liquid spirit is in circulation. The dehydrating material is very cheap and the losses of alcohol are less than 0.5 per cent. Conversion costs (in Cuba, 1934) for dehydrating from 94 per cent to 99.8 per cent product were calculated as one-half cent per gallon of alcohol.

A process that combines the use of solid or liquid absorbents with fractional distillation is described by Du Bois.[71] The method takes advantage of the fact that anhydrous alcohol can be obtained in a single operation by distillation of aqueous alcohol provided its concentration is above the azeotropic point (97.2 per cent). Thus, in practice, part of the high strength alcohol (98 per cent or over) is returned to the distillation tower so that the concentration of alcohol therein is above that of the azeotropic mixture. The vapors are then dehydrated with a solid absorbent in another vessel and again returned in part to the distilling column. Economical operation calls for maximum heat recovery. The final product is reported to be substantially free of water. It is further stated that this modified absorbent method can compete advantageously with azeotropic distillation.

In the Hiag process,[72] ascending wet alcohol vapors are sprayed with a solution, or suspension, of dehydrating salts (sodium acetate, alone or mixed with potassium acetate). The dried vapors, when condensed, furnish a 99.8 per cent alcohol. The aqueous-alcoholic solution of the salts is freed from alcohol in a small column. Water is removed from the hydrated salts in a regenerator by heating indirectly with superheated steam at 300°C. The dried salt is then passed into a vessel containing absolute alcohol and returned to the dehydrating tower for further use.

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[67] J. Barbaudy and A. Lalande, *Ann. combustibles liquides*, 1930, **5**, 795; *Chem. Zentr.*, 1931, **2**, 1211; *Chem. Abs.*, 1930, **24**, 5595; *Brit. Chem. Abs.* **A**, 1930, 1356.

[68] S. Sosnowski and E. Treszczanowicz, *Przemysl Chem.*, 1936, **20**, 69; *Chem. Abs.*, 1936, **30**, 7943.

[69] P. Pusl, *International Sugar J.*, 1933, **35**, 346; *Chem. Abs.*, 1933, **27**, 4341; *Brit. Chem. Abs.* **B**, 1934, 38. Also T. Wallis, *Petroleum Z.*, 1934, **30**, No. 41, 3; *J. Inst. Pet. Tech.*, 1934, **20**, 584A. British P. 394,086, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 172; *Brit. Chem. Abs.* **B**, 1933, 822.

[70] E. Lühder, *Z. Spiritusind.*, 1934, **57**, 67; *Chem. Abs.*, 1934, **28**, 5919.

[71] G. Du Bois, *Chim. & ind.*, 1933, **30**, 535; *Brit. Chem. Abs.* **B**, 1933, 953; *Chem. Abs.*, 1934, **28**, 2117.

[72] V. Siedler, *Petroleum Z.*, 1934, **30**, No. 36, 1; *J. Inst. Pet. Tech.*, 1934, **20**, 526A. Also, *International Sugar J.*, 1933, **35**, 266. Used by Holzverkohlungs-industrie A.-G.

A process in which lime is employed under pressure as a drying agent[73] is also practiced commercially.[74] Kyrides[75] suggests the use of alkali alkoxides or phenoxides for the dehydration of aqueous alcohols. For example, absolute ethyl alcohol may be prepared by the action of disodium glycolate on a water-ethanol mixture.

ETHYL ALCOHOL AS A FUEL

The addition of certain proportions of ethyl alcohol to motor fuels has been made compulsory by law in many countries, nominally for the purpose of assisting agriculture and of furthering economic nationalism. The relative merits and demerits of this alcohol as a constituent of motor blends have been described in numerous trade journals as well as scientific reports. Only a relatively brief summary of the salient features of the problem is possible in a book of this character. Discussion of the voluminous literature on the use of ethanol in gasoline-alcohol mixtures will be found in Chapter 44.

Alcohol Fuels in Paste Form. A minor use of alcohol is in the form of so-called "gels" where heat production is required only for short periods. For this purpose Fleming[76] incorporates 3 parts of nitrocellulose (insoluble in alcohol) in a solution of 2 parts of an alcohol-soluble nitrocellulose in 95 parts of ethanol. Citric acid may be included (in small quantity) as an antigelating agent.

McBain[77] disperses 3 per cent of an insoluble (under normal conditions) nitrocellulose in ethyl alcohol at —30 to —60°C. The colloidal solution is then warmed to room temperature. The resultant gel may be used as "canned fuel."

An unusual, white, opaque, aqueous, alcoholic gel containing ethanol and having a tendency to crystallize has been prepared by Henstock.[78] This was done by adding the alcohol to an aqueous solution of potassium ethyl sulphate. The composition was represented by the formula,

$$KC_2H_5SO_4 \cdot 6H_2O \cdot 6C_2H_5OH$$

It persists for 48 hours at 15°C. but crystallizes rapidly at higher temperatures. Its precipitation from aqueous solutions by alcohol has been recommended as a means of identifying potassium ions.

ETHYL ALCOHOL AS A CHEMICAL INTERMEDIATE

Ethyl alcohol is extensively used as a raw material for the production of a wide variety of organic chemicals, including diethyl ether, ethyl esters, acetaldehyde, crotonaldehyde, normal butanol, acetic acid and acetic anhydride, as well as ethylated bases such as ethyl aniline.

ETHERS FROM ETHANOL

Diethyl ether is obtained in considerable quantities as a by-product when ethyl alcohol is made from ethylene by the sulphuric acid absorption method, as already noted.

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[73] R. Fritzweiler and K. R. Dietrich, *Proc. World Petr. Congr.*, 1933, 2, 784; *J. Inst. Pet. Tech.*, 1934, 20, 258A.

[74] Merck & Co.

[75] L. P. Kyrides, U. S. P. 1,907,834, May 9, 1933, to Monsanto Chem. Co., *Brit. Chem. Abs.* B, 1934, 86; *Chem. Abs.*, 1933, 27, 3774.

[76] J. S. B. Fleming, British P. 394,696, 1933, to Imperial Chemical Industries Ltd.; *Chem. Abs.*, 1934, 28, 292; *Brit. Chem. Abs.* B, 1933, 773.

[77] J. W. McBain, U. S. P. 1,934,725, Nov. 14, 1933, to S. Sterman & Co.; *Chem. Abs.*, 1934, 28, 882; *Brit. Chem. Abs.* B, 1934, 745.

[78] H. Henstock, *Trans. Faraday Soc.*, 1935, 31, 446; *Brit. Chem. Abs.* A, 1935, 297; *Chem. Abs.*, 1935, 29, 2820.

A determination of the boiling point of specially purified diethyl ether has been made by the U. S. Bureau of Standards,[79] and found to be 34.481 ± 0.003°C. The *dt/dp* ratio for ether, in degrees per mm. at 760 mm. of mercury, is given as 0.0372.

This ether may be produced by the anhydration of ethyl alcohol by means of numerous catalysts. Yields up to 45 per cent were reported when ethanol was heated below 300°C. with anhydrous aluminum sulphate, alumina or thoria. It is also reported that the following materials[80] were effective catalysts: copper sulphate, tin chloride, manganous chloride, aluminum chloride, potash and chrome alum and chromium sulphate.

Similar procedures were followed by Brown and Odell[81] using alumina at pressures above atmospheric and heating the alcohol above its critical temperature. Another process[82] furnishes ethers and alcohols from olefins and liquid water by use of the same catalyst. Normal pressure is effective at temperatures above 100°C., but at 250 to 365°C. more than 10 atmospheres were necessary. In the latter case the higher temperature was reported for alcohol formation. Operation at 250°C. favored ether formation as did increasing the ratio of olefin to water.

It has been proposed[83] to carry out the production of ethers from alcohols in two successive stages. In the first, aqueous ethanol is passed (oxidizing gases being excluded) over alumina, iron oxide or chromium oxide at about 300°C. The olefin produced is at once converted into ether by passage over a second catalyst, used at 50-400°C., and composed of metallic salts, such as sulphates and chlorides, activated by a silver salt. Both conversions take place at normal pressure.

Kosolapov[84] studied the anhydration of alcohol with mixed catalysts prepared by ammoniacal precipitation of nitrates of alumina (with additions of iron, calcium or vanadium) followed by activation at 360°C. The pyrolytic reactions resulted in the formation of some methane and ethane as well as aldehydes, but no hydrogen, in gaseous mixture along with the normally produced ethylene. Kosolapov thinks breaking up of the alcohol molecule by catalysts may be as indicated by the following reactions:

$$\begin{aligned} 2C_2H_5OH - 2H_2O &\longrightarrow CH_3CH{=}CHCH_3 \longrightarrow 2C_2H_4 \\ 2C_2H_5OH - H_2O &\longrightarrow CH_3CHOHCH_2CH_3 \longrightarrow CH_3CHO + C_2H_6 \\ C_2H_5OH &\longrightarrow HCHO + CH_4 \end{aligned}$$

Adadurov and Krainii[85] made a similar study using, at 300 to 400°C., contact agents of alumina deposited in varying amounts on charcoal. The rate of ethylene formation at 350°C. was increased by eighteen times after an 8-fold increase in concentration of alumina. A similar multiplication by 45 occurred when pure catalyst without carrier was utilized.

The anhydration reaction may also be carried out in the presence of liquid acid catalysts such as sulphuric acid. According to Schumann and Ufer,[86] ether may be continuously distilled off while contacting a vaporous mixture of concentrated

[79] M. Wojciechowski. *J. Research Natl. Bur. Standards*. 1936. 17. 459 (*Research Paper No.* 922); *Chem. Abs.*, 1936, **30**, 7929.

[80] British P. 350.010. 1930; *Brit. Chem. Abs.* **B**, 1931, 917; add'n to British P. 332,756, 1929; *Brit. Chem. Abs.* **B**, 1930. 981; both to Bataafsche Petroleum Maatschappij.

[81] R. L. Brown and W. W. Odell. U. S. P. 1.873.536 and 1.873.537, Aug. 23, 1932; *Chem. Abs.*, 1932, **26**, 5962, 5964; *Brit. Chem. Abs.* **B**, 1934, 617.

[82] R. L. Brown and W. W. Odell. U. S. P. 1.907.317. May 2, 1933; *Brit. Chem. Abs.* **B**, 1934, 86; *Chem. Abs.*, 1933, **27**, 3481.

[83] French P. 782,760, 1935, to Crima soc. anon.; *Chem. Abs.*, 1935, **29**, 6902. Also British P. 445,963, 1936; *Brit. Chem. Abs.* **B**, 1936, 823; *Chem. Abs.*, 1936, **30**, 6760.

[84] Z. E. Kosolapov, *J. Gen. Chem. Russ.*, 1935, **5**, 307; *Brit. Chem. Abs.* **A**, 1935, 1104; *Chem. Abs.*, 1935, **29**, 6206.

[85] I. E. Adadurov and P. Y. Krainii, *J. Phys. Chem. Russ.*, 1934, **5**, 136; *Chem. Abs.*, 1935, **29**, 31.

[86] G. Schumann and H. Ufer, U. S. P. 1,961,987, June 5, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 4748.

aqueous alcohol with ethylsulphuric acid (and a small amount of sulphuric acid as catalyst) at a temperature above 100°C. (See Fig. 99.)

Alcohol from Ether. The transformation of ethyl alcohol into ether and water is, of course, a reversible reaction. Vansheidt and Lozovskii[87] found that diethyl ether could be hydrolyzed, after 2 to 4 hours' treatment, to the extent of 70 per cent by heating with 5-25 per cent aqueous sulphuric acid at 200°C. The yield of ethyl alcohol was considerably lessened by the use of more concentrated sulphuric acid or if the temperature was allowed to exceed 230°C. (Under similar conditions no hydrolysis resulted from use of phosphoric acid.)

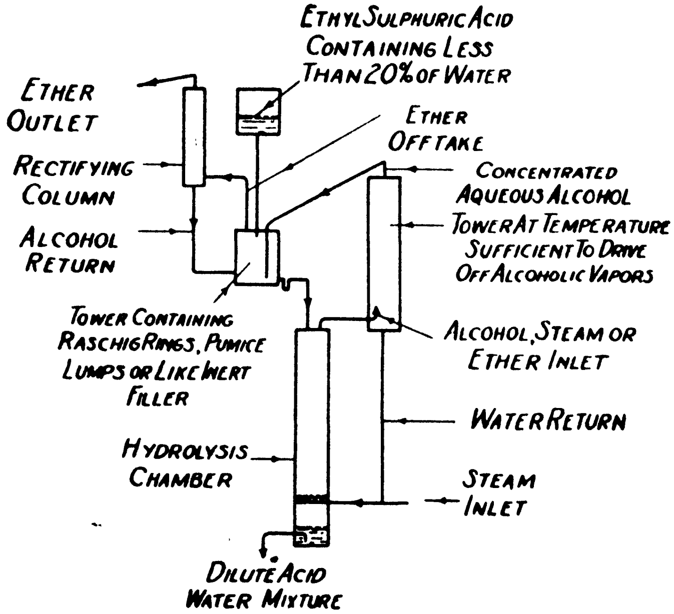
Ethyl Sulphuric Acid Containing Less Than 20% of Water
Ether Outlet
Ether Offtake
Rectifying Column
Concentrated Aqueous Alcohol
Alcohol Return
Tower At Temperature Sufficient To Drive Off Alcoholic Vapors
Tower Containing Raschig Rings, Pumice Lumps or Like Inert Filler
Alcohol, Steam or Ether Inlet
Water Return
Hydrolysis Chamber
Steam Inlet
Dilute Acid Water Mixture

FIG. 99.—Sketch of Method for Continuous Production of Ether from Ethylsulphuric Acid and Ethanol. (C. Schumann and H. Ufer)

Semerano[87a] investigated the equilibria of the reaction at temperatures of 249°

$$2C_2H_5OH \rightleftharpoons (C_2H_5)_2O + H_2O$$

and 266°C. and pressures of 10 to 70 atmospheres. A mixture of the oxide and phosphate of aluminum was employed as a catalyst. The use of high pressures made it possible to maintain the quantities of alcohol or ether which decomposed into ethylene and water within very narrow limits. It was found that the reaction was favored by increasing the temperature and decreasing the pressure. From calculations based on the equilibrium constants at atmospheric pressure it was concluded that at 249° and 266°C., approximately 85 per cent of the alcohol can be etherified.

An alumina catalyst prepared by neutralizing an aqueous alkaline solution of sodium aluminate with nitric acid was found by Kagan and his co-workers[88] to be much superior to alumina prepared by Willstätter's method as regards activity in promoting the hydration of diethyl ether. Passage of a mixture of ether with 2.5 parts of water vapor over this alumina catalyst at 325°C. furnished 22.5 per cent of ethyl alcohol, 6 per cent of ethylene, and a residue of unchanged ether.

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[87] A. Vansheidt and M. Lozovskii. *J. Gen. Chem. Russ.*, 1933, **3**, 329; *Chem. Abs.*, 1934, **28**, 2323; *Brit. Chem. Abs.* **A**, 1933, 1252.

[87a] G. Semerano, *Gazz. chim. ital.*, 1936, **66**, 162; *Chem. Abs.*, 1937, **31**, 931.

Since the production of ethyl ether as a by-product has accompanied the development of synthetic methods for the manufacture of ethanol from olefins, it has become desirable to convert ether to alcohol. As has been noted above, this can be done by contacting the ether with mineral acids under certain conditions of temperature and pressure. Lewis[89] suggests use of pressure greater than 225 lb. per sq. in. and a temperature of about 270°C. in order to supply alcohol of high purity in good yields. As a catalyst, 10 per cent sulphuric acid is recommended. Other acids, e.g., hydrochloric (5 to 6 per cent), and phosphoric (15 to 20 per cent), or salts such as chlorides of aluminum or zinc (which are acidic in dilute aqueous solutions), may function as contact materials. Two or more catalysts may be present and promoters may be added, such as metallic silver or oily substances (mineral or fatty oils or Turkey-red oil).

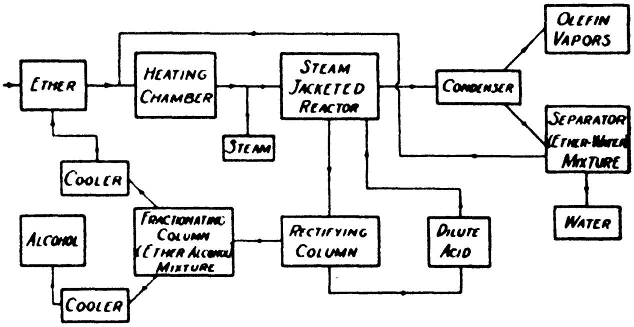

FIG. 100.—Flow Diagram for Conversion of Ethers to Alcohols. (W. K. Lewis)

The best operating temperature is between 240 and 260°C. since higher temperatures result in formation of olefin instead of alcohol.

A major requirement of the process is the application of sufficient pressure to prevent evaporation of water from the aqueous catalyst. The lower limit seemed to be about 225 lbs. per sq. in. at 200°C., but from 500 to over 1000 lbs. per sq. in. may be used. With a fairly high pressure, the alcohol may be retained in the liquid phase and recovered from the dilute liquid catalyst by distillation, after reduction of pressure. For example, at 250°C. with a pressure of 2000 lbs. per sq. in., using a 10 per cent sulphuric acid catalyst, the acid liquor withdrawn contained 20 to 22 per cent alcohol and practically no alcohol was found in the vapor discharged at the time.

In another instance, ether was vaporized and passed into a reaction vessel containing 10 per cent sulphuric acid heated to a temperature of 272°C. Ether vapor was then continuously supplied to maintain a pressure of 2000 lbs. per sq. in.

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[88] M. Y. Kagan, I. M. Rossinskaya and S. M. Cherntzov, *J. Gen. Chem. Russ.*, 1933, **3**, 337; *Chem. Abs.*, 1934, **28**, 2323; *Brit. Chem. Abs.* **A**, 1933, 1252.

[89] W. K Lewis, U. S. P. 2 045 785, June 30, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 5589. British P. 456,547, 1936; *Brit. Chem. Abs.* **B**, 1937, 31; *Chem. Abs.*, 1937, **31**, 2229.

during a contact period of 25 minutes. The acid liquor withdrawn at the end of this time contained 22 per cent ethyl alcohol. The latter was recovered from the acid by distillation at normal pressure and represented a conversion of over 90 per cent of the ether fed into the system. On increasing the time of reaction to 100 minutes, alcohol concentration fell to 16 per cent and an equivalent amount of ethylene was found in the exit gases. It was shown that the time of contact required for reaction could be greatly reduced by increasing the agitation or degree of contact between the acid and the ethers. See Fig. 100.

On the other hand, high pressures (1000-5000 lbs. per sq. in.) and a temperature of 250-350°C. have been proposed[90] for the conversion of ethanol into diethyl ether.[91] A non-oxidizing inorganic acid, e.g., phosphoric acid, is added to the alcohol which circulates in a flow system, both alcohol and acid being maintained in the liquid phase.

A number of other catalysts for the hydrolysis of diethyl ether to ethanol have been investigated.[92] In each instance, vapors of ether and water were generated separately and then passed jointly over the contact agents at 280-350°C. Ferric oxide was not effective, but oxides of zinc, magnesium and aluminum were increasingly active in the order named. Mixtures of oxides were even better, those of aluminum and iron being most efficient and those of aluminum and magnesium and of aluminum and zinc being less so. In the absence of water, ether decomposed to ethylene, aluminum oxide being the most active catalyst in this case.

Thermal Decomposition. An apparatus has been described[93] for studying the kinetics of homogeneous gas reactions at high temperatures and at pressures of several hundred atmospheres. The rate of decomposition of diethyl ether at 426°C. was found to increase rapidly with pressures up to 10,000 cm., and then more slowly. At 14,500 cm. the value attained was approximately 50 times that assumed for infinite pressure. These results seemed to indicate that the number of degrees of freedom varies with the time between molecular collisions. A more accurate investigation[94] of the kinetics of the ether decomposition at pressures up to 260 atmospheres confirmed the previous results[95] and showed that they cannot be brought about by a simple unimolecular change. At the highest pressures used the rate of reaction was still increasing. On the basis of the Rice-Herzfeld free radical mechanism,[96] a qualitative explanation of the data was thought possible, but the reaction was considered too complicated to allow any quantitative comparison with theoretical values.

The formation of olefin and water by the decomposition of diethyl ether vapor on bauxite at 150-300°C. has been investigated by Marx.[97] He used a closed apparatus with continuous circulation of gas. With high ether pressure at the beginning of an experiment and a relatively small volume of catalyst, the activating material adsorbed ether to such an extent that the reaction was retarded by the water formed. This effect was eliminated by circulating the gases over barium oxide. The initial absorption was then followed by a decomposition in two stages: the principal reaction (of the order 0.35)[98] during which ether in the vapor phase was continuously supplied to the bauxite as the action progressed, and a second interval (of the order 3) when the decomposition of the material adsorbed at the active centers took place.

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[90] M. R. Fenske, U. S. P. 2,045,560, June 23, 1936; *Chem. Abs.*, 1936, 30, 5589.

[91] V. A. Kireev and E. M. Khachadurova have reported the boiling points of various mixtures of ethyl alcohol and diethyl ether at atmospheric pressure, also the compositions of the alcohol-ether mixtures in vapor phase. *J. Applied Chem.* (*U.S.S.R.*), 1934, 7, 495; *Chem. Abs.*, 1935, 29, 2061; *Brit. Chem. Abs.* A, 1934, 1301.

[92] N. Kozlov and N. Golubovskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1936, 6, 1506; *Chem. Abs.*, 1937, 31, 2166; *Brit. Chem. Abs.* A, 1937, 1, 144.

[93] E. W. R. Steacie and E. Solomon, *J. Chem. Physics*, 1934, 2, 503; *Brit. Chem. Abs.* A, 1934, 1179; *Chem. Abs.*, 1934, 28, 6614.

[94] E. W. R. Steacie, W. H. Hatcher and S. Rosenberg, *J. Chem. Physics*, 1936, 4, 220; *Brit. Chem. Abs.* A, 1936, 568; *Chem. Abs.*, 1936, 30, 2830.

[95] E. W. R. Steacie and E. Solomon, *loc. cit.*

[96] See F. O. Rice and K. K. Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, 1935.

[97] W. Marx, *Z. physik. Chem.*, 1933, B23, 33; *Brit. Chem. Abs.* A, 1933, 1252; *Chem. Abs.*, 1934, 28, 2322.

When the experimental conditions were reversed so that a large amount of catalyst was present and the initial vapor pressure quite low, the concentration of the reactant on the activating material was small. Two intermediate steps were then evident: one of zero order[99] corresponding with diffusion from the gas phase and another (of order 1 to 2) during which ether is supplied by the inactive surface.

Both normal and retarded reactions had the same heat of activation, calculated as 31 kg. cal. per mole of diethyl ether. The number of active centers was estimated to be between 2×10^{19} and 10^{20}.

Jaeger[100] reports anhydration of ethanol at 340-380°C. by a sodium-aluminum-borotitanate containing thoria. Other base-exchange materials that have been acid-leached so that the active components are in nonexchangeable form may also be used as catalysts in similar dehydrating reactions.

Deterioration of Anesthetic Ether. In the presence of air, diethyl ether rapidly forms peroxides[100a] and their decomposition products. These substances may be removed from ether, according to Christiansen and Van Winkle,[101] by means of active charcoal (in the absence of oxygen). The addition of a small quantity of a cuprous compound such as cuprous oxide has been recommended for avoiding deterioration during storage.[102] The conversion of diethyl ether into acetaldehyde and a small proportion of acetic acid and its anhydride has been reported by Dreyfus.[103] The reaction took place on heating in the presence of an oxidation or of a dehydrogenation catalyst to 300 or 450°C. By working in the liquid phase, the reaction products could be oxidized to acetic acid.

A study of the deterioration of anesthetic ether has been made by Manikov and Larionov[104] for the purpose of discovering stabilizers and testing their value. They found the commonly used solid potassium hydroxide to be effective against formation of aldehydes and peroxide compounds for 9 months with ether stored in opaque containers but for only 19 days if the liquid was exposed to daylight. In the dark, iron shavings retarded peroxide production and increased slightly the aldehyde content of the samples. In diffused light, ether broke down considerably more rapidly in presence of reduced iron than of the ordinary metal. Preliminary tests indicated storage over solid potassium hydroxide in bottles covered with black paper as the best practical method of preservation. Further work by Goryainova[105] disclosed that any stabilizing effect of iron is possible only when the ether is free from the products of peroxide reduction that are present after the usual purification process. It was found that the anesthetic could be kept without change for 8 to 9 months without use of a stabilizer, if it had been freed from aldehydes and peroxides by partial oxidation with alkaline permanganate followed by treatment with alkaline potassium manganate. Following such purification, iron turnings served to prolong the preservation period considerably.

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[98] When the decomposition of only one substance is concerned: A reaction of the order n is one in which the rate of decomposition of the original reactant at any time is proportional to the nth power of its concentration at that time.

[99] A reaction of zero order is one in which the rate of reaction is independent of the concentration(s) of the reacting substance(s).

[100] A. O. Jaeger, U. S. P. 1,914,722, June 20, 1933, to Selden Co.; *Brit. Chem. Abs.* **B**, 1934, 136; *Chem. Abs.*, 1933, **27**, 4238.

[100a] H. King, *J.C.S.*, **1929**, 738; *Brit. Chem. Abs.* **B**, 1929, 971; *Chem. Abs.*, 1929, **23**, 3661.

[101] W. G. Christiansen and R. Van Winkle, U. S. P. 1,971,930, Aug. 28, 1934, to E. R. Squibb & Sons; *Brit. Chem. Abs.* **B**, 1935, 715; *Chem. Abs.*, 1934, **28**, 6532.

[102] W. G. Christiansen and R. Van Winkle, U. S. P. 1,813,664, July 14, 1931, to E. R. Squibb & Sons; *Brit. Chem. Abs.* **B**, 1932, 414; *Chem. Abs.*, 1931, **25**, 5176.

[103] H. Dreyfus, French P. 753,168, 1933; *Chem. Abs.*, 1934, **28**, 776. British P. 401,269, 1932; *Brit. Chem. Abs.* **B**, 1934, 136.

[104] A. Manikov and Z. Larionov, *Org. Chem. Ind.* (*U.S.S.R.*), 1936, 1, 161; *Chem. Abs.*, 1936, **30**, 5361.

[105] N. S. Goryainova, *Org. Chem. Ind.* (*U.S.S.R.*), 1936, 1, 162; *Chem. Abs.*, 1936, **30**, 5361.

Lott[106] suggests purification of commercial ether by dephlegmation to remove alcohol. He recommends further treatment at 40-50°C. with mercuric oxide by using the latter in aqueous suspension in order to obtain better contact between the ether and the metallic oxide. Cox and Greer[107] advocate that after treatment with sulphuric acid or chlorine and with a bisulphite solution (or oxide of mercury), for aldehyde removal, the ether fraction be subjected to the action of a strong alkali, for example, sodium hydroxide.

In this connection Arup[108] obtained 0.9 per cent residue after active distillation (on a water bath) of a sample of ether which had been kept in dark storage for over 3 years. Another test showed the liquid material to contain available oxygen equivalent to 0.4 per cent hydrogen peroxide. The residue mentioned above exploded violently at 124°C. Similar residues were non-explosive if the ether had been treated with silver hydroxide,[109] dry silver oxide, or if butter fat (0.1 per cent) had been added prior to the evaporation.

Degering[110] notes the tendency to stress the fire-hazard of ether while neglecting the explosive properties of the substance when peroxides are present. He found ethyl, isopropyl and butyl ethers full of peroxides. For testing he uses a slightly acid solution of potassium iodide, shaking equal volumes of it and the ether together (1 cc. of each). If any iodine is liberated, the ether should be purified. He recommends for purification, the addition of 1 volume of 20 per cent sodium hydroxide to 200 volumes of ether, followed by steam distillation of the ether layer.

Williams[111] reports all ethers studied by his organization[112] to have developed peroxides on storage and that, with practically all, explosions have been experienced. He considers the dry distillation of any ether hazardous unless peroxides have been proved absent. Even a small amount becomes concentrated toward the end of a distillation. Any mechanical shock increases the likelihood of explosion. Distillation of "suspected" ethers with steam and maintaining an excess of water with the still residues is recommended for rendering the peroxides harmless.

The use of inhibitors is discussed by Williams, though he does not consider them infallible. He recommends that distillations of any ether should be carried out to dryness only from the safe side of a shatter-proof screen, as the peroxide explosions are usually extremely violent.

The danger attendant on making extractions in the laboratory with peroxide-containing ethers is emphasized by MacCulloch,[113] of the Government Medical Store Depot at Madras, India. It is stated that consignments of several cwt. of ether in 4-oz. bottles would arrive entirely unfit for anesthetic use due to its readiness to develop complex decomposition compounds. Many tests developed the fact that a copper wire (guage #20) placed in an amber storage bottle up to the height of the contents is a preventive for such deterioration. MacCulloch notes that ether protected thus in 1931 had as yet (1936) developed no peroxides.

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[106] W. A. Lott, U. S. P. 2,056,972, Oct. 13, 1936, to E. R. Squibb & Sons; *Chem. Abs.*, 1936, **30**, 8241.

[107] H. L. Cox and P. S. Greer, U. S. P. 2,050,600, Aug. 11, 1936, to Union Carbide and Carbon Corp.; *Chem. Abs.*, 1936, **30**, 6766.

[108] P. S. Arup, *Chem. & Ind.*, **1936**, 546; *Chem. Abs.*, 1936, **30**, 6563; *Brit. Chem. Abs.* **A**, 1936, 963.

[109] E. A. Werner, *Analyst*, 1933, **58**, 335; *Brit. Chem. Abs.* **A**, 1933, 809; *Chem. Abs.*, 1933, **27**, 3912.

[110] E. F. Degering, *J. Chem. Ed.*, 1936, **13**, 494.

[111] E. C. Williams, *Chem. & Ind.*, **1936**, 580.

[112] The Shell Development Company Laboratories at Emeryville, California.

[113] A. F. MacCulloch, *Chem. & Ind.*, **1936**, 964.

In 1934, the "Stores" method of anesthetic preservation was altered to the addition of 1 in 5000 of hydroquinone. This renders the ether unsuitable for use in analytical laboratories, however. The presence of copper wire introduces no weighable matter into the substance and avoids the purification necessary before peroxidized ethers can be utilized safely.

In this connection, steel wire, iron filings or precipitated metallic iron have been recommended to inhibit ether decomposition in tin-plated containers used for storage and shipment of the compound.[114]

In the recovery of volatile solvents by adsorbing their vapors in active carbon, it has been noted that traces of peroxides were found only after extended exposure of the saturated adsorbent to atmospheric oxygen.[115] Formation of ethyl peroxides did not occur when alcohol-ether vapor was adsorbed by, or desorbed from, active carbon, regardless of whether iron or oxygen was present.

HIGHER ALCOHOLS AND ESTERS (OR ACIDS) FROM ETHANOL

It has long been known that ethyl alcohol can be readily dehydrogenated catalytically to acetaldehyde in the presence of metals (e.g., copper) at temperatures of 200-300°C. It has been shown that, in addition to acetaldehyde, such substances as *n*-butanol and ethyl acetate may be obtained directly by the decomposition of ethyl alcohol by means of certain specific catalysts. Dolgov and Volnov[116] investigated the decomposition of ethyl alcohol vapor at 450°C. by means of a mixture of the oxides of iron and aluminum precipitated on powdered animal charcoal. A fair yield of *n*-butanol was secured together with various other products, including mixed gases, formaldehyde, acetone, olefins, acetaldehyde, diamyl ether and dibutyl ether. The formation of butanol was interpreted as proceeding according to the equations:

$$C_2H_5OH \longrightarrow C_2H_4 + H_2O$$

and

$$C_2H_5OH + C_2H_4 \longrightarrow C_4H_9OH$$

Secondary reactions, viz.,

$$C_2H_5OH \longrightarrow CO + CH_4 + H_2$$
$$2C_2H_5OH \longrightarrow CO_2 + 3CH_4$$

were considerably checked by activation of the catalyst with lanthanum oxide. With this promoter 22 per cent yields of butanol were possible at 450°C. Lower temperatures decreased the yield of butanol.

DIRECT CONVERSION OF ALCOHOL TO ESTERS

Relatively large conversions of ethyl alcohol into alkyl acetate have been achieved by passage of the former as vapor over copper oxide containing small proportions of difficultly reducible metallic oxides. Thus, Ivannikov and Gavrilova[117] obtained 24 per cent of ethyl acetate when using copper oxide impregnated with 0.1-0.2 per cent of thoria as the contact agent and a temperature of 350°C. The formation of this ester, which reaction could be inhibited by the addition of acetic acid, was regarded as occurring through the condensation of acetaldehyde initially formed. By conducting ethyl alcohol vapor over a copper catalyst, prepared from cupric acetate and containing 0.2 per cent of ceria,[118] Dolgov and his collaborators[119] obtained a 33 per cent yield of ethyl acetate at 275°C. and atmospheric pressure. After returning the gas mixture four times over the catalyst at 250°C., analysis showed the presence of 40 per cent ethyl acetate, 20 per cent acetic acid and 15.5 per cent acetaldehyde. The most active catalyst was one deposited on granular carbon. In further experiments by the same workers,[120] repeated recirculation of the reaction products effected yields of 45 per cent ethyl acetate, 24 per cent acetic acid and 11 per cent acetaldehyde. These results were considered exceptional on comparison with those of 20 per cent ester formation reported by others for similar conversions.

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[114] F. W. Nitardy, U. S. P. 2,058,250, Oct. 20, 1936, to E. R. Squibb & Sons; *Chem. Abs.*, 1937, 31, 217.

[115] E. V. Alekseevskii and G. M. Moskvin, *J. Appl. Chem.* (*U.S.S.R.*), 1936, 9, 1010; *Brit. Chem. Abs.* A, 1936, 1196.

[116] B. N. Dolgov and J. N. Volnov, *J. Gen. Chem. Russ.*, 1933, 3, 313; *Brit. Chem. Abs.* B, 1933, 953; *Chem. Abs.*, 1934, 28, 2322.

[117] P. Y. Ivannikov and E. Y. Gavrilova, *J. Chem. Ind.* (*Moscow*), 1935, 12, 1256; *Chem. Abs.*, 1936, 30, 2171; *Brit. Chem. Abs.* A, 1936, 571.

In a detailed study[121] of the factors influencing direct esterification of alcohols the probable mechanism of the reactions involved is discussed by these same investigators.

The catalyst was prepared by slowly introducing cupric acetate solution (containing 0.2 per cent ceric nitrate) into hot concentrated sodium hydroxide solution: the precipitate was washed, dried at 105°C. and reduced with hydrogen at 180-200°C. The material loses one-third of its activity in 18 days and more than half in 28 days. However, it is completely restored by oxidation in dry air at 180-200°C., followed by re-treatment which hydrogen. Substitution of pulverulent for granular carbon as a base for the catalyst decreased ester formation.

Dilution of the ethanol used, beginning with 10 per cent of water, cut down the yields of both ester and acid. Ninety-five per cent ethyl alcohol seemed industrially practical as a raw material.

The effect of each reactant on the catalyst was tested by use of standard reagents treated under esterification conditions. Only the aldehyde had a destructive action.

Distillation of the condensate from treatment of ethanol resulted in the formation of several azeotropic mixtures. At 68-72°C., there was collected a solvent containing 72 per cent acetate and 25 per cent alcohol, but no acid or aldehyde. Ninety-five per cent acetaldehyde had been completely removed by distillation at 20-22°C. A small amount of higher esters (mostly butyl acetate) passed over at 85-90°C. The final fraction, boiling point 110-118°C., consisted of 100 per cent acetic acid; no residue was left in the flask.

Dolgov and his co-workers consider the reaction for ester formation to be that reported by Tishchenko:[122]

$$\begin{aligned}&(1)\quad C_2H_5OH \longrightarrow CH_3CHO + H_2\\&(2)\quad 2CH_3CHO \longrightarrow CH_3CO_2C_2H_5\end{aligned}$$

Attendant small amounts of acetal appearing after single runs could be accounted for by the equation suggested by Geuther:[123]

$$CH_3CHO + 2C_2H_5OH \rightleftharpoons CH_3CH(OC_2H_5)_2 + H_2O$$

Technological problems of large scale procedure according to the method developed by Dolgov and his collaborators are discussed by Beizel, Hel'ms and Lel'chuk.[124]

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[118] P. Y. Ivannikov and A. V. Zherko, *J. Applied Chem.* (*U.S.S.R.*), 1933, **6**, 1148; *Chem. Abs.*, 1934, **28**, 4036; *Brit. Chem. Abs.* B, 1934, 231.

[119] B. N. Dolgov, M. M. Koton and S. L. Lel'chuk, *J. Chem. Ind.* (*Moscow*), 1935, **12**, 1066; *Chem. Abs.*, 1936, **30**, 1027; *Brit. Chem. Abs.* B, 1936, 181.

[120] B. N. Dolgov, M. M. Koton and S. D. Lel'chuk, *J. Gen Chem.* (*U.S.S.R.*), 1935, **5**, 1611; *Brit. Chem. Abs.* B, 1936, 536; *Chem. Abs.*, 1936, **30**, 2174.

[121] B. N. Dolgov, M. M. Koton and S. D. Lel'chuk, *Org. Chem. Ind.* (*U.S.S.R.*), 1936, **1**, 70; *Chem. Abs.*, 1936, **30**, 5178.

[122] V. E. Tishchenko, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 355, 482; *Chem. Zentr.*, 1906, **2**, 1309, 1552; *J.C.S.*, 1907, **92** (1), 182.

[123] Geuther, *Ann.*, 1863, **126**, 62.

It was found impractical to recirculate the reaction products on account of poisoning the catalyst by the aldehyde. The latter is to be distilled off at 20-22°C. so that the unchanged alcohol, 40 per cent of the original, can be re-used. On the basis of this recovery, 1 ton (metric) of 95 per cent ethyl alcohol is expected to produce, in a single run, 550 to 600 kg. of solvent ester, 350 kg. acetic acid, 40 to 50 kg. acetal and 25 kg. of gas (97 per cent hydrogen).

Contact decomposition of ethyl alcohol to form hydrogen and acetaldehyde with subsequent condensation of the latter to produce ethyl acetate has been accomplished by Bukreeva-Prozorovskaya and Yanuisheva.[125] At 250°C., the condensate was composed of 60-64 per cent ethyl acetate, 3-6 per cent acetic acid and 3-6 per cent acetaldehyde.

A variation of the above general method of forming organic esters has been found by Guinot[126] to result in reduced yields of acetaldehyde in the final product. Vapors of the primary aliphatic alcohol are passed over a dehydrogenation catalyst maintained at 200-260°C. After a partial condensation of the vapors leaving the reaction chamber, the remaining gases, rich in hydrogen, are continuously recirculated, with additions of fresh alcohol, as needed, through the catalyzing furnace. Reduced copper, carrying titania, thoria or urania as a promoter, functioned as the activator in the production of ethyl acetate from ethanol.

A synthesis of propionic acid from ethanol was attempted by Hardy.[127] Using 200 atmospheres pressure he passed alcohol, carbon monoxide and steam through 87 per cent phosphoric acid containing 2 per cent copper phosphate. Between temperatures of 250 and 370°C., he obtained a product consisting of high-boiling isomers of ethylene, water, ethanol, small amounts of propionic acid and ethyl propionate together with traces of acetaldehyde and volatile hydrocarbons. The polymers of ethylene were formed two or three times as rapidly as the propionic acid. It was thought that pressures of 500 to 1000 atmospheres might give more favorable results.

It may be noted that Ivannikov and Gavrilova[128] find a copper-uranium catalyst suitable for obtaining 50 per cent yields of esters from propanol and butanol. The contact material functions at 220°C. and slowly loses its activity. The reactions are analagous to the above described production of ethyl acetate and hydrogen from ethanol by use of copper catalysts with small additions of ceria or thoria.

The production of butanol from ethanol is effected by Fuchs and Querfurth[129] by passage of ethanol vapor, admixed with hydrogen, over a catalyst containing magnesia and a smaller proportion of copper. Butanol and also higher alcohols are obtained[130] by passage of a similar mixture of ethyl alcohol and hydrogen at 200-350°C. over a catalyst of magnesia containing a smaller amount of another metal or metallic oxide, such as chromic oxide. For example, hexyl, octyl and higher alcohols and ethers were produced by passage of ethanol, butanol and hydrogen in mixture over a catalyst composed of metallic copper, alumina and magnesia. The temperature of the treatment was 350°C. and the pressure maintained was 30 atmospheres. In another case, acetaldehyde and hydrogen, contacted with alumina, calcium oxide and copper at 260°C., gave a mixture of butanol, butyl propionate, butyl acetate and higher alcohols.

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[124] N. M. Beizel, I. E. Hel'ms and S. L. Lel'chuk, *Org. Chem. Ind.* (*U.S.S.R.*), 1936, 1, 102; *Chem. Abs.*, 1936, 30, 5178.

[125] L. M. Bukreeva-Prozorovskaya and Z. S. Yanuisheva, *Sintet Kauchuk*, 1936, No. 3, 13; *Chem. Abs.*, 1936, 30, 7539.

[126] H. M. Guinot, French P. 798,842, 1936, to Usines de Melle (Soc. anon.); *Chem. Abs.*, 1936, 30, 7584.

[127] D. V. N. Hardy, *J.C.S.*, 1936, 358; *Chem. Abs.*, 1936, 30, 3776; *Brit. Chem. Abs.* A, 1936, 590.

[128] P. Y. Ivannikov and E. Y. Gavrilova, *J. Applied Chem.* (*U.S.S.R.*), 1936, 490; *Chem. Abs.*, 1936, 30, 7539.

[129] O. Fuchs and W. Querfurth, U. S. P. 1,992,480, Feb. 26, 1935, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1935, 29, 2550. British P. 364,134, 1930; *Brit. Chem. Abs.* B, 1932, 459.

[130] O. Fuchs and W. Querfurth, German P. 594,672, 1934, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1934, 28, 4430. British P. 381,185, 1932; *Chem. Abs.*, 1933, 27, 3943. French P. 42,154, 1933; *Chem. Abs.*, 1933, 27, 4813; add'n to 722,052; *Chem. Abs.*, 1932, 26, 4062.

Higher alcohols and esters are obtained by passage of certain oxygenated derivatives of paraffins (esters, aldehydes and alcohols other than ethanol or its mixture with methanol) and hydrogen at ordinary or increased pressures over mixed catalysts.[131] The latter consisted of one or more feebly basic oxides. A number of substances were effective for this purpose, viz., alumina, uranium oxide and thoria, in admixture with not more than 10 per cent of copper, silver, nickel or chromium. In some cases the addition of a basic oxide, such as lime, barium oxide, magnesia or lithia, is helpful. Pressures of 1 to 50 atmospheres and temperatures ranging from 150 to 400°C. may be employed. Herrmann[132] describes the conversion of ethyl alcohol into a mixture of acetaldehyde, butanol, acetone, ethyl acetate, ethylene and hydrogen. The ethanol is passed in vapor form at atmospheric pressure over a catalyst consisting of a compound of manganese, magnesium, zinc, iron, barium, strontium, calcium, sodium or copper. The temperature necessary, 420-460°C., is above that best suited to the production of acetaldehyde.

The action of a specially treated dehydrogenating catalyst in combination with a condensing agent has been described by Scott[133] for the conversion in *one stage* of alcohols either to those of higher molecular weight or to esters of the original reactant. One catalyst[134] found effective for making butanol or ethyl acetate from ethanol consisted of a copper compound supported on alumina gel and reduced in hydrogen; at 200 to 240°C., if to be used for ester formation, or at 400 to 550°C. for the production of higher alcohols. In the latter case, the condensing agent, e.g., carbonate of potassium or cesium, is added in a ratio of 1 part to 2 parts catalyst for combination of only 2 molecules of the starting material (alcohol). Higher proportions are necessary for the formation of higher alcohols.

A reaction temperature of 200-230°C. favored longer life of the catalyst and hence its control of the desired end product. The conversions reported were carried out in the liquid phase in a steel bomb, agitated for periods varying from 4 to 22 hours. The pressures used ranged from 150 to 1000 lbs. per sq. in., dependent upon the boiling points of the liquids present and the temperatures employed. Higher alcohol formation was favored by about 100 lbs. per sq. in. added hydrogen. Ester production with hydrogen as a by-product required venting the gas as formed.

Anhydrous alcohols were employed, but supplementary experiments showed that the presence of up to 10 per cent of water did not prevent formation of satisfactory quantities of the end products.

Thus, by heating 450 cc. of dry ethyl alcohol with 35 g. of a reduced catalyst to 220°C. for 22 hours, under pressure, 97 per cent of the alcohol decomposed was transformed into ethyl acetate. A similar treatment at 200°C. was carried out in the presence of the same catalyst after addition of 20 g. of potassium carbonate as condensing agent. Under a hydrogen partial pressure of 100 lbs. per sq. in., 65 per cent of the ethyl alcohol was converted into butanol, 17 per cent into hexanol, 14 per cent into higher alcohols and small amounts of ethyl acetate. Primary or secondary alcohols as well as mixtures were found to respond to this one-stage treatment. It was necessary, however, always to have present two hydrogen atoms on the carbon atom next to the one combined with the hydroxyl group. The following condensations were recorded:

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[131] W. P. Joshua, H. M. Stanley and J. B. Dymock, British P. 393,267, 1933, to British Industrial Solvents, Ltd.; *Chem. Abs.*, 1933, 27, 5754; *Brit. Chem. Abs.* B, 1933, 777.

[132] W. O. Herrmann, German P. 615,073, 1935, to Chemische Forschungsges.m.b.H.; *Chem. Abs.*, 1935, 29, 6252.

[133] N. D. Scott, U. S. P. 2,004,350, June 11, 1935, to E. I. du Pont de Nemours and Co.; *Chem. Abs.*, 1935, 29, 4381. British P. 424,284, 1935; *Brit. Chem. Abs.* B, 1935, 442; *Chem. Abs.*, 1935, 29, 4381.

[134] Another material for this purpose was prepared by hydrogen gas reduction of a copper chromite catalyst described by H. Adkins and R. Connor, *J.A.C.S.*, 1931, 53, 1092; *Brit. Chem. Abs.* A, 1931, 598; *Chem. Abs.*, 1931, 25, 1808.

Alcohols Used as Starting Materials	Condensation Products
Normal propanol	2-Methyl-pentanol-1 *plus* water
Normal butanol	2-Ethyl-hexanol-1 *plus* water
Ethanol and *n*-propanol	*n*-and "active" amyl alcohols *plus* the usual condensates from the separate alcohols
Isopropyl alcohol	2-Methyl-pentanol-4 *plus* water
Cyclohexanol	Cyclohexyl-cyclohexanol *plus* water
Normal propanol	Propyl propionate *plus* hydrogen

PYROLYSIS OF ESTERS

That the simple ethers are not readily dehydrated to produce olefins is common knowledge A study of the pyrolysis of esters and acetals and certain related substances by Bilger and Hibbert[135] has established some important facts which have a bearing on the chemistry of alcohols and their derivatives:

1. "Ester pyrolysis and reverse reactions are best explained by the 'radical theory' as developed and extended from Nef's dissociation theory."

2. According to experimental evidence "ester pyrolysis does not progress through ether intermediates" and "the olefin derivative comes solely from the alkoxy portion of the ester."

3. "The stability of isomeric esters toward heat is greater for those derived from primary than from secondary alcohols."

4. "Methyl esters, or substituted methyl esters, are much more stable towards heat than either ethyl esters, β-substituted ethyl esters, or the higher alkyl esters."

Results on pyrolysis of ethyl acetate and the isomer ethylene acetal appear in Table 70.

TABLE 70.—*Data on Pyrolysis of Ethyl Acetate and an Isomeric Acetal.*

Material pyrolyzed	Ethyl Acetate	Ethylene Acetal
Temperature	485°C.	485°C.
Total time	65 min.	65 min.
Contact period in hot zone	1.2 min.	1.2 min.
Products obtained:		
Ethylene (moles)	0.174	0.023
Acid (moles)	0.176	0.005
Percentage decomposition:		
into Ethylene	76.6	10.2
into Acid	77.8	2.3

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[135] E. M. Bilger and H. Hibbert, *J.A.C.S.*, 1936, **58**, 823; *Brit. Chem. Abs.* **A**, 1936, 821; *Chem. Abs.*, 1936, **30**, 4816.

OTHER REACTIONS OF ETHYL ALCOHOL

The conversion of ethyl alcohol into liquid hydrocarbons and other products by the action of heat and pressure has been investigated by Smolenski.[136] Whereas gases were chiefly obtained at 350°C. under pressure, upwards of 80 per cent of liquid products were produced at 400°C. but these consisted mainly of oxygenated compounds. Treatment at 450°C. resulted in a 40 per cent yield of liquids containing a substantial proportion of cyclic hydrocarbons. In the presence of alumina at this temperature, 20-25 per cent of the alcohol was transformed into hydrocarbons, mainly aromatic, though admixed with some naphthenes.

Alkali metal ethylates are obtained by treatment of ethyl alcohol with the alkali metals, hydrogen being evolved. It has been shown by Williams and Bost[137] that, in the absence of water, the reaction between ethyl alcohol and sodium hydroxide was 75-100 per cent complete according to the equation,

$$C_2H_5OH + NaOH \rightleftharpoons C_2H_5ONa + H_2O,$$

after the alcohol-hydroxide mixture had been boiled for 1 hour. Alkali metal alcoholates prepared, for example, by the reaction between dry ethyl alcohol and sodium hydroxide, may be precipitated from the reaction mixture by the use of anhydrous acetone.[138] The mixture is either refluxed or held at room temperature until crystals are formed. The latter may be washed with kerosene and dried in air free from moisture and carbon dioxide.

At high temperatures ethyl alcohol reacts with caustic alkalies with elimination of hydrogen to yield alkali metal acetates. One procedure[139] for making sodium acetate is that of passing ethyl alcohol vapor, at 250-300°C., into a fused equimolecular mixture of alkali hydroxides and acetates. The alkali used is a mixture of sodium and potassium hydroxides in molecular ratios varying from 1:2 to 3:1. After dissolving the reaction mass in water, sodium acetate trihydrate is recovered by crystallization. The mother liquor is evaporated to dryness and the residue fused with more sodium hydroxide for further use.

Aluminum ethylate, and alcoholates generally, are finding important industrial applications, particularly as catalysts in certain organic reactions. A review of the preparation and properties of these interesting compounds has been contributed by Zappi and Restelli,[140] who prepared aluminum alcoholates by the method of Henle.[141] They found that well-cleaned aluminum filings begin to react with anhydrous alcohols at room temperature if mercuric chloride is present. Solubilities in the corresponding alcohols were determined for the alcoholates prepared from the following: methanol, ethanol, propanol (α- and β-), butanol (α- and β-), phenyl methanol and β-propenol. With the exception of the first and last given, the solubilities ranged from 12 to 47 per cent.

Another procedure for the production of aluminum ethoxide, or ethylate, consists in the action of metallic aluminum on ethanol, used slightly in excess.[142] The reaction is carried out at 120°C. in an autoclave. The product may be recovered by vacuum distillation. A yield of 95 per cent is reported as being obtained without the aid of catalysts. According to Seib,[143] the same compound may be made by starting the interaction between metal and alcohol in the presence of a small amount of the alcoholate to be produced. In this instance, the addition should be less than one-fifth of the yield of aluminum ethoxide to be expected from the alcohol treated.

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[136] K. Smolenski. *Internat. Congr. Pure and Applied Chem., Madrid*, Apr. 5-11. 1934; *Brennstoff-Chem.*, 1934. **15**, 212. See also, K. Smolenski and S. Kowalewski. *Bull. Acad. Polonaise*, 1934, **A**, 304; *Brit. Chem. Abs.* **A**, 1935, 193; *Chem. Abs.*, 1935, **29**, 1060.

[137] D. Williams and R. W. Bost, *J. Chem. Physics*, 1936, **4**, 251; *Chem. Abs.*, 1936, **30**, 3402; *Brit. Chem. Abs.* **A**, 1936, 703.

[138] E. T. Olson and R. H. Twining, U. S. P. 1,978,647, Oct. 30, 1934. to Cleveland Cliffs Iron Co.; *Chem. Abs.*, 1935, **29**, 179; *Brit. Chem. Abs.* **B**, 1936. 273.

[139] C. J. Strosacker. C. C. Kennedy and E. L. Pelton, U. S. P. 1,961,625, June 5. 1934, to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1935, 899; *Chem. Abs.*, 1934, **28**, 4844.

[140] E. V. Zappi and E. Restelli, *Andes asoc. quim. Argentina*, 1934, **22**, 87; *Chem. Abs.*, 1935, **29**, 1383; *Brit. Chem. Abs.* **A**, 1935. 325.

[141] F. Henle, *Ber.*, 1920, **53**, 719; *Chem. Abs.*, 1920, **14**, 2601; *J.S.C.I.*, 1920, **39**, 501A.

[142] Consortium für elektrochemische Industrie G.m.b.H., British P. 454,480, 1936; *Brit. Chem. Abs.* **B**. 1936, 1193; *Chem. Abs.*, 1937, **31**, 1043.

Alcohols and Sulphuric Acid. With sulphuric acid, or pyrosulphuric acid, ethyl alcohol combines to form ethylsulphuric acid, the amount of the latter substance produced being controlled by the equilibrium,

$$C_2H_5OH + H_2SO_4 \rightleftharpoons C_2H_5O \cdot SO_3H + H_2O$$

This reaction was studied by Suter and Oberg[144] who determined the equilibrium constants for ethanol and 96.7 per cent acid at 25 and 35°C.; these values for the lower temperature as well as the extent of esterification for a molar ratio of one are given in Table 71. The value of K (equilibrium constant) for ethyl alcohol and 96.7 per cent sulphuric acid at 35°C. was 1.84.

TABLE 71.—*Reaction of Ethyl Alcohol with Sulphuric Acid at 25°C.*

Acid	Per Cent of $C_2H_5SO_4H$	K
96.7% H_2SO_4	52.6	1.76
H_2SO_4 + 5.2% SO_3	59.8	2.02
H_2SO_4 + 22.6% SO_3	65.1	2.08
H_2SO_4 + 31.98% SO_3	67.7	1.98

The activities of ethylene in concentrated sulphuric acid and of ethanol in dilute sulphuric acid are known from the work of Gallagher and Keyes.[145]

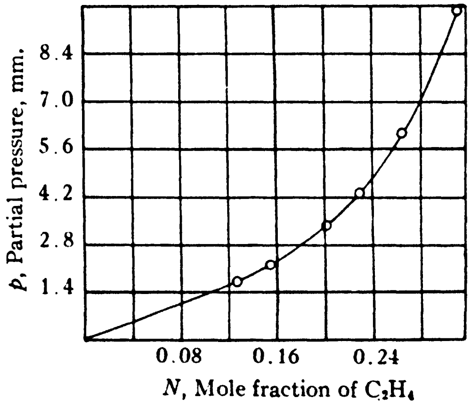

FIG. 101.
Partial Pressures of Ethylene in Equilibrium with Concentrated Sulphuric Acid. (M. Gallagher and D. B. Keyes)

Courtesy Journal of American Chemical Society

The results obtained in a series of carefully checked experiments on specially purified materials are shown in Tables 72 and 73. They are plotted graphically in Fig. 101 and 102. In each case the figures in the first column are the mole fractions of the solutions, given as moles of solute per mole of solution. The partial pressures of the olefin (or alcohol) appear in the second column. Under the con-

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[143] J. Seib, German P. 602,376, 1934 to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1935, **29**, 478.

[144] C. M. Suter and E. Oberg, *J.A.C.S.*, 1934, **56**, 677; *Brit. Chem. Abs.* **A**, 1934, 509; *Chem. Abs.*, 1934, **28**, 2672.

[145] M. Gallagher and D. B. Keyes, *J.A.C.S.*, 1934, **56**, 2221; *Brit. Chem. Abs.* **A**, 1935, 34; *Chem. Abs.*, 1935, **29**, 664.

TABLE 72.—*The Activity of Ethylene in Concentrated Sulphuric Acid (Acid of 95.4 Per Cent Concentration).*

N Mole Fraction of Ethylene	p Partial Pressure of Ethylene mm.	Henry's Law Constants K (P/N)	a Activity of Ethylene
0.3122	9.541	30.56	0.7376
0.2674	6.037	22.57	0.4662
0.2307	4.294	18.61	0.3318
0.2039	3.339	16.38	0.2578
0.1561	2.160	13.84	0.1668
0.1280	1.658	12.95	0.1280

TABLE 73.—*The Activity of Ethanol in Diluted Sulphuric Acid. (Acid of 62.81 Per Cent Concentration).*

N Mole Fraction of Ethanol	p Partial Pressure of Ethanol mm.	Henry's Law Constants K (P/N)	a Activity of Ethanol
0.2400	60.85	254	0.2953
0.1685	41.77	248	0.2027
0.1274	27.65	217	0.1342
0.0805	16.76	208	0.0814
0.0584	12.11	207	0.0588
0.0382	7.84	205	0.0381

ditions of experimentation, the investigators considered that the activities of the solute could be determined from the partial pressures above the solution, as shown by Lewis and Randall,[146] or in this case

$$a = p/K = pN'/p'$$

when N' and p' are the mole fraction and the partial pressure at infinite dilution. Henry's law constant was taken as the value for the most dilute solution, i.e., the last value in the third column in the case of ethylene and as the average of the last two corresponding values for ethanol.

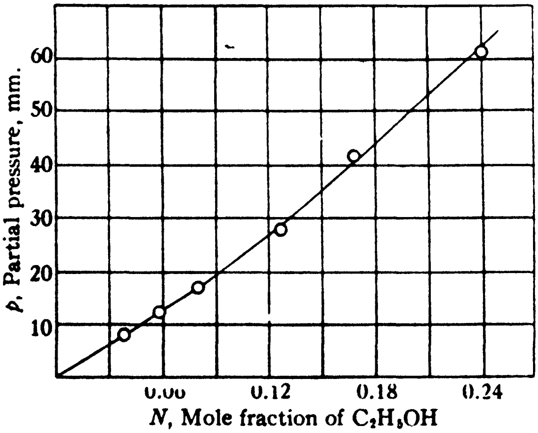

FIG. 102. Partial Pressures of Ethanol in Equilibrium with Diluted Sulphuric Acid. (M. Gallagher and D. B. Keyes)

Courtesy Journal of American Chemical Society

$$K = p'/N' = \begin{cases} 12.95 \text{ (for ethylene)} \\ \text{or } 206 \text{ (for ethanol)} \end{cases}$$

[146] G. N. Lewis and M. Randall. "Thermodynamics," McGraw-Hill Book Company, New York, 1923.

Alcohol and Hydrogen Halides. The preparation of alkyl chlorides by vapor-phase combination of alcohols with hydrogen chloride in the presence of certain catalysts is discussed by Ernst.[147] For example, vaporized ethanol and hydrogen chloride formed ethyl chloride at 240-300°C. when passed over activated carbon which had been impregnated with phosphoric acid.

According to Brooks,[148] ethyl chloride is formed when dry hydrogen chloride reacts with diethyl ether in the presence of anhydrous metallic halide catalysts, such as the chloride of zinc, aluminum or ferric iron. The method of procedure recommended is the passage of the reactants in vapor form over the catalysts. The latter require periodic renewal since they are so chosen as to absorb the water formed in the reaction. Another method for accomplishing the same result is to treat a suspension of the metallic chloride (in ether) with the hydrogen halide gas at a temperature below the boiling point of the ethyl chloride. The temperature used in either case must be below that required to expel water from the catalyst chosen.

An "autothermal" method of reacting ethyl alcohol with a hydrogen halide to produce ethyl chloride has been described by Holt and Daudt.[149] For example, alcohol and hydrogen chloride are passed under definite conditions into a solution of zinc chloride which has its concentration below the equilibrium value at the operating temperature. At 138-140°C. (the equilibrium concentration being 80 per cent) a 70 per cent solution is held constant by allowing the required amount of water vapor to return to the catalytic liquor from the evolved reaction vapors.

By means of a halide of bismuth as catalyst, yields of over 90 per cent ethyl chloride are reported from ethanol and hydrogen chloride.[150] The activator may be used in solution or supported on pumice. Bismuthyl chloride, or the tribromide of bismuth, has been used, e.g., in 70 to 90 per cent aqueous solution. The temperature is held above 110°C., to remove water continuously in vapor form.

In the preparation of ethyl bromide by reaction of ethyl alcohol, sulphuric acid and sodium bromide, the addition of small proportions of metallic copper is said[151] to increase the yield from 57 per cent to 80 per cent. The function of the copper appears to be associated with its reducing action which serves to limit the bromine to its ionic state. No free bromine appeared when the copper was used.

Another process for production of alkyl halides from ethers consists in treating the latter with certain organic halides,[152] viz. those having no hydrogen attached to a carbon next to that combined with the halogen. A small percentage of the corresponding alcohol may be included in the ether. Alumina in granular form or as a gel may serve as the catalyst. Phosphates of cerium, iron, cadmium or aluminum are also mentioned for this purpose. The temperature of reaction is between 270 and 340°C. Chloroform, carbon tetrachloride, di-iodomethane, dichlorophenyl methane or trichloroacetic acid are among the organic halides adapted for furnishing the necessary halogen atoms in the above conversion.

Diethyl thiosulphite, $(C_2H_5)_2S_2O_2$, has been prepared by Meuwsen[153] by the action of sulphur monochloride on sodium ethylate according to the following metathesis:

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[147] P. Ernst, German P. 583,477, 1933, to Alexander Wacker Ges. für elektrochemische Industrie G.m.b.H.; *Chem. Abs.*, 1934, **28**, 1052. U. S. P. 1,937,269, Nov. 28, 1933; *Chem. Abs.*, 1934, **28**, 1052; *Brit. Chem. Abs.* **B**, 1934, 824.

[148] B. T. Brooks, U. S. P. 2,015,706, Oct. 1, 1935, to Standard Alcohol Co.; *Brit. Chem. Abs.* **B**, 1936, 1140; *Chem. Abs.*, 1935, **29**, 8004.

[149] L. C. Holt and H. W. Daudt, U. S. P. 1,983,542, Dec. 11, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 817; *Brit. Chem. Abs.* **B**, 1935, 1085.

[150] H. W. Daudt, U. S. P. 2,016,075, Oct. 1, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 8004; *Brit. Chem. Abs.* **B**, 1936, 1140. British P. 450,843, 1936; *Chem. Abs.*, 1937, **31**, 114; *Brit. Chem. Abs.* **B**, 1936, 971.

[151] P. Hendrixson, *Proc. Iowa Acad. Sci.*, 1934, **41**, 165; *Chem. Abs.*, 1935, **29**, 3650; *Brit. Chem. Abs.* **A**, 1936, 52.

[152] British P. 452,934, 1935 to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1936, 1140.

[153] A. Meuwsen, *Ber.*, 1935, **68**, 121; *Chem. Abs.*, 1935, **29**, 2506; *Brit. Chem. Abs.* **A**, 1935, 326.

$$S_2Cl_2 + 2NaOC_2H_5 = (C_2H_5)_2S_2O_2 + 2NaCl$$

The alcoholate used was free from alcohol. The reaction was carried out in a medium of well cooled low-boiling petroleum ether (b.p. 30-40°C.). The ester formed, a greenish-yellow liquid boiling at 62.0-62.7°C. at 16 mm. pressure, was stable to air and moisture. A colorless liquid, considered an isomer and boiling at 67-68°C. at 16 mm. pressure, was obtained by vacuum distillation of the colored product.

Ethyl chlorosulphinate, $SOCl{\cdot}OC_2H_5$, was also prepared. It boiled at 45°C. with 38 mm. pressure and at 171°C. under normal conditions. No isomer was obtained.

Ethyl hypochlorite[154] has been recognized by Suknevich and Chilingaryan[155] as the first product of the action of calcium hypochlorite on ethyl alcohol. The subsequent formation of chloral in this reaction is regarded by these investigators as proceeding according to the following sequence of changes:

$$\begin{gathered} C_2H_5OCl \longrightarrow HCl + CH_3CHO \longrightarrow CH_2{=}CHOH \xrightarrow{C_2H_5OCl} \\ CH_2ClCH(OH)OC_2H_5 \longrightarrow CHCl_2{\cdot}CHO \longrightarrow CCl_3CHO \end{gathered}$$

Deanesly[156] describes the formation of the hypohalites of primary, secondary or tertiary alcohols by introducing a halogen into a mixture of alcohol and aqueous alkali in equivalent proportions, the reaction proceeding as follows:

$$KOH + ROH + Cl_2 \longrightarrow ROCl + KCl + H_2O$$

Ethyl Alcohol and Amines. Ethyl alcohol may be combined with primary and secondary amines under the influence of certain catalysts with the formation of ethylated bases and elimination of water. Catalysts, consisting of alumina, or alumina admixed with other metallic oxides, have been tried for the ethylation of ammonia in the vapor phase.[157] The same results were obtained at 300-400°C. and at atmospheric pressure in the presence of alumina alone or alumina plus 10 per cent ferric oxide. The latter iron catalyst, however, yielded less gaseous by-products. In the direct ethylation of aniline by ethyl alcohol in the vapor phase at 350-400°C. and atmospheric pressure, both mono- and diethylanilines are formed. The results of a series of experiments[158] using a mixture of 1 mole of aniline and 1.45 moles of alcohol are summarized in Table 74.

Adkins and Cramer[159] recommend a catalyst of reduced nickel for the interaction of ethyl alcohol and tertiary heterocyclic amines. For example, ethanol (1 mole) and piperidine (0.5 mole), at a temperature of 200°C. and pressure of 100 atmospheres in the presence of this contact agent, furnished an 80 per cent yield of N-ethyl piperidine. Under similar conditions α-methyl piperidine and the alcohol gave an 84 per cent yield of N-ethyl-α-methyl piperidine.

As catalysts for the direct combination of alcohols with ammonia, or a primary

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[154] For discussion of the properties and uses of these hypochlorites see Chapter 25.

[155] I. F. Suknevich and A. A. Chilingaryan, *Ber.*, 1935, **68**, 1210; *Chem. Abs.*, 1935, **29**, 5808; *Brit. Chem. Abs.* **A**, 1935, 958.

[156] R. M. Deanesly, U. S. P. 1,938,175. Sept. 26, 1932, to Shell Development Co.; *Chem. Zentr.*, 1934, 1, 1709, *Brit. Chem. Abs.* **B**, 1934, 824.

[157] N. I. Shuikin, A. A. Balandin and Z. I. Plotkin. *J. Gen. Chem.* (*U.S.S.R.*), 1934, **4**, 1444; *Chem. Abs.*, 1935, **29**, 3584; *Brit. Chem. Abs.* **A**, 1935, 742; 1936, 169.

[158] N. I. Shuikin, A. A. Balandin and F. T. Duimov, *J. Gen. Chem.* (*U.S.S.R.*), 1934, **4**, 1451; *Chem. Abs.*, 1935, **29**, 3585. *J. Phys. Chem.* (*U.S.S.R.*), **1935**, 1207; *Brit. Chem. Abs.* **A**, 1936, 169.

[159] H. Adkins and H. I. Cramer, U. S. P. 2,058,547, Oct. 27, 1936; *Chem. Abs.*, 1937, **31**, 110.

TABLE 74.—*Direct Combination of Ethyl Alcohol and Aniline*

Additions to Alumina Catalyst	Optimum Conversion Temperature	Per Cent Aniline Reacted	Yield	
			Monoethyl Aniline	Diethyl Aniline
None..............	350°C.	67.5	64.3	3.2
Fe_2O_3 (10 per cent)..	375°C.	52.9	52.2	0.7
SnO (10 per cent)...	375°C.	50.2	48.7	1.5
Cr_2O_3 (20 per cent)..	375°C.	43.2	43.2	Trace
NiO (5 per cent)....	350°C.	38.5	38.4	0.1
ZnO (10 per cent)...	350°C.	31.6	31.6	Trace

or secondary amine, phosphoric acid or a phosphate dispersed on a carrier has been suggested.[160] Reaction was effected at 250-500°C. in the vapor phase. The use of oxides, chlorides or sulphates of copper and iron, in the presence of acids or alkaline salts, has also been described for the same purpose.[161]

Other Reactions. Catalytic hydrogenation of toluene by means of ethanol has been accomplished by Shuikin and Feder.[162] When mixed vapors of toluene and ethyl alcohol were led over a nickel-alumina catalyst at 170-210°C., the former substance was hydrogenated and the latter dehydrogenated in accordance with the following reaction:

$$\underset{\text{toluene}}{C_6H_5CH_3} + \underset{\text{ethanol}}{3C_2H_5OH} \rightleftharpoons \underset{\substack{\text{methyl}\\\text{cyclohexane}}}{C_6H_{11}CH_3} + \underset{\text{acetaldehyde}}{3CH_3CHO}$$

The workers considered the most favorable temperature for this metathesis to be 190°C. The best yield was 26 per cent of the theoretical based on an aldehyde-toluene ratio of 9:1. Similar results were possible at 180-190°C. with a catalyst formed by precipitation of platinum on asbestos.

The effect of the electric arc or spark on ethanol vapor has been reported by Petrik.[163] Using zinc electrodes he obtained a mixture of highly calorific gases. The compositions of the yields varied considerably as may be seen from the following figures: hydrogen, 30 to 58 per cent; methane, 6.7 to 29 per cent; carbon monoxide, 22 to 29 per cent; olefins, 9 to 12 per cent.

In the catalytic production of bivinyl (butadiene) directly from ethyl alcohol by the method of Lebedev,[164] *o*-ethylphenol has been identified[165] in the hydrocarbon condensate along with other homologous phenols. Among the by-products of the same conversion further work[166] has disclosed normal primary saturated alcohols of the pentane and hexane series.

THERMAL DECOMPOSITION OF ETHYL ALCOHOL

The catalytic decomposition of ethanol has been studied by Boomer and Morris.[167] Equimolecular proportions of the alcohol and water were passed in vapor form through a vertical autoclave containing the catalyst. The temperatures used were 350, 400, 450 and 500°C. The contact agent was prepared by impregnating silica gel[168] with a concentrated solution of cupric and chromic chlorides (in equimolar proportions) and then drying at 100°C. Afterwards the mass was transferred to a pyrex glass tube and treated with hydrogen for 5 hours at 300°C.

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[160] British P. 399,201, 1932, to Röhm and Haas Co.; *Brit. Chem. Abs.* B, 1933, 998; *Chem. Abs.*, 1934, **28**, 1715. French P. 734,404, 1932; *Chem. Abs.*, 1933, **27**, 995.

[161] French P. 767,771, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 474.

[162] N. I. Shuikin and E. A. Feder, *J. Applied Chem. (U.S.S.R.)*, 1934, **7**, 1192; *Chem. Abs.*, 1935, **29**, 5819; *Brit. Chem. Abs.* A, 1935, 334.

[163] F. Petrik, *Chem. Obzor.*, 1934, **9**, 43; *Chem. Zentr.*, 1935, **1**, 181; *Brit. Chem. Abs.* B, 1935, 660; *Chem. Abs.*, 1934, **28**, 5341.

[164] S. V. Lebedev, British P. 331,482, 1929; *Chem. Abs.*, 1931, **25**, 115; *Brit. Chem. Abs.* B, 1930, 939. See also Chapter 4.

[165] M. V. Likhosherstov, A. A. Petrov and S. V. Alekseev, *J. Gen. Chem.* (*U.S.S.R.*), 1934, **4**, 1274; *Chem. Abs.*, 1935, **29**, 3298; *Brit. Chem. Abs.* B, 1935, 442.

[166] S. V. Lebedev, G. G. Koblyanskii, N. Z. Andreev, I. K. Gorn, I. A. Livshitz, G. N. Sibiryakova and Ya. M. Slobodin, *Truдui Gosudarst. Opuit. Zavoda Sintet. Kauchuka, Litera B. III. Synthetic Rubber*, 1934, 41; *Chem. Abs.*, 1936, **30**, 4810.

[167] E. H. Boomer and H. E. Morris, *Can. J. Research*, 1930, **2**, 384; *Chem. Abs.*, 1930, **24**, 4451; *Brit. Chem. Abs.* A, 1930, 1268.

The workers were interested mainly in the appearance of ethane in the gases resulting from the pyrolysis of alcohol. They made no analysis of the small amounts of oily, acidic, aqueous products, which were collected in a water-cooled receiver followed by a condenser maintained at the temperature of a solid-carbon-dioxide-ether mixture. While water vapor exerted a retarding effect on the speed of reaction, it passed through the catalyst unchanged. The gaseous products were analyzed for hydrogen and carbon monoxide (by burning with copper oxide), for methane and ethane (by slow combustion with oxygen) and for carbon dioxide. The results appear in Table 75.

TABLE 75.—*Gaseous Products from Alcohol Pyrolysis Over a Copper-Chromium-Silica Gel Catalyst.*

	Percentage Composition of Gases					
Temp. in °C.	Hydrogen	Carbon Monoxide	Ethylene	Carbon Dioxide	Methane	Ethane
350	6.0	0.7	90.3	0.5	0.7	1.8
400	23.5	0.9	70.0	2.7	0.9	2.1
450	29.4	0.9	53.0	8.6	4.9	3.2
500	40.5	0.9	30.4	10.2	11.2	6.4

Although the catalyst obviously changed from a promoter of dehydration at 350°C. to one possessing dehydrogenation powers at 500°C., the yield of ethane, hydrogen and carbon dioxide increased while that of ethylene decreased. This did not seem to favor a conclusion that the ethane was formed by hydrogenation of ethylene. Carbon was not deposited on the catalyst and the source of the carbon dioxide was not thought to be carbon monoxide. The results appeared to call for further investigation. A series of twenty catalysts, mostly binary, containing nickel and chromium or copper, were prepared and tested for their action on ethyl alcohol solutions in water.[169] The two main types of reaction involved were dehydrogenation and dehydration of the ethanol molecule as indicated in the equations:

$$C_2H_5OH = CH_3CHO + H_2$$
$$C_2H_5OH = C_2H_4 + H_2O$$

Comparison of a large number of runs, carried out as in the previously reported work, indicated that with nickel and chromium mixtures, the combinations behave as two chemical individuals, each having its characteristics dependent upon relative concentrations and mode of preparation. Mixture effects, as such, were confined to secondary reactions and any promoter-effect of one metal on the other in the initial decompositions was either absent entirely or very slight. The apparent order of resistance of the catalysts to deactivation was copper, chromium, nickel. The dehydrating action of the chromium was always apparent. Reactivity and nature of the resultant reactions depended, in general, on the method of preparation of the contact material, chromium requiring severe treatment for activation at all times. The type of reducing agent used had a decisive effect on the secondary reactions in some cases. The most active catalysts for the primary decompositions usually were also effective for the formation of by-products. The action of the nickel always predominated. Subsidiary changes, resulting in the production of carbon, carbon dioxide and complex organic liquids (not analyzed), occurred in practically all cases.

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[168] For the preparation of the silica gel, see H. N. Holmes and J. A. Anderson, *Ind. Eng. Chem.*, 1925, 17, 280; *J.S.C.I.*, 1925, 44, 399B; *Chem. Abs.*, 1925, 19, 1217.

[169] E. H. Boomer and H. E. Morris, *Can. J. Research*, 1932, 6, 471; *Chem. Abs.*, 1932, 26, 4532; *Brit. Chem. Abs.* A, 1932, 819.

Boomer and Morris[170] have also described experiments in which the temperature was carried up to 500°C. and addition of water or carbon dioxide to the ethanol vapor was practiced to reduce the space velocity of the gaseous alcohol. This was possible since carbon dioxide has been shown to have practically no effect and water vapor a repressing action, if any, upon the primary reactions.

Formation of Methane. A catalyst prepared by the ignition of nickel nitrate on asbestos promoted the aldehydic decomposition reaction. The aldehyde in turn was converted (by thermal decomposition) into methane and carbon monoxide, the latter giving free carbon and carbon dioxide (see Table 76). Similar results were attained with a nickel chromate contact mass.

TABLE 76.—*Thermal Decomposition of Equimolecular Solution of Alcohol and Water with a Nickel Catalyst.*

Temp., °C.	Composition of Gaseous Products Per Cent by Volume						
	CO_2	CO	Total as CO	CH_4	H_2	C_2H_6	C_2H_4
300	0.8	25.7	27.3	28.6	40.9	4.0	Nil
375	19.5	5.5	44.5	42.5	30.0	2.5	Nil
400	21.8	3.4	47.0	50.0	24.7	Nil	Nil
450	23.4	4.4	51.0	48.6	23.6	Nil	Nil
500	20.6	2.0	43.2	45.2	32.2	Nil	Nil

It was believed that the methane came directly from decomposed aldehyde and that hydrogenation of carbon monoxide or dioxide was inappreciable.

However, the hydrogenation reaction was promoted by other catalysts prepared as follows:

A. Four moles chromic oxide, 1 mole zinc oxide, 0.5 mole alumina with traces of copper powder and sodium carbonate. After mixing, grinding to a paste and drying, the very hard material was treated with hydrogen at 300-350°C.

B. One mole zinc oxide, 1 mole chromic oxide, 0.5 mole cupric oxide with a trace of copper powder, treated as above.

C. An equimolar mixture of potassium chromate, nickel nitrate and ferric nitrate were co-precipitated in slightly alkaline solution, the liquor decanted, the precipitate washed, dried at 110°C., and reduced at 300-350°C.

The results secured with these activators appear in Table 77. The liquid prod-

TABLE 77.—*Thermal Decomposition of Equimolecular Solutions of Alcohol and Water with Hydrogenation Catalysts.*

Catalyst Used	Temp., °C.	Composition of Gaseous Products Per Cent by Volume				
		CO_2	H_2	CH_4	CO	C_2H_4
A	400	10.0	85.5	2.3	Nil	2.1
	500	14.4	78.0	2.3	Nil	5.3
B	400	9.5	86.2	1.6	Nil	2.7
	500	10.4	84.2	1.6	Nil	3.8
C	350	7.3	91.2	Nil	Nil	1.5
	450	18.8	77.8	Nil	Nil	3.4

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[170] E. H. Boomer and H. E. Morris, *Can. J. Research*, 1934, **10**, 743; *Chem. Abs.*, 1934, **28**, 4972; *Brit. Chem. Abs.* **A**, 1934, 1199.

ucts contained a high-boiling oily fraction. The absence of free carbon formation was considered to render the ethylene an unlikely source of methane and the most reasonable mechanism for its presence was held to involve hydrogenation of carbon dioxide. Both these gases (hydrogen and carbon dioxide) were present in large proportions and their interaction is not inhibited by water. Results with catalyst C (when any aldehyde formed was obviously not decomposed and the ethylene not polymerized) seemed to verify the above conclusions especially as this catalyst did not even hydrogenate the carbon dioxide to produce methane.

Formation of Ethane. The two reactions considered as possible explanations for the presence of ethane (during pyrolysis of alcohol) were both found by Boomer and Morris to occur in proportions controlled by experimental conditions:

1. Hydrogenation of the primary product, ethylene, by nascent hydrogen.[171]
2. Autoxidation and reduction of the alcohol, giving ethane directly.[172]

$$2C_2H_5OH = CH_3CHO + H_2O + C_2H_6$$

A comparison of results obtained in treatment of absolute alcohol with those secured when water vapor or carbon dioxide gas were present is given in Table 78. The same catalyst was used in each case, viz., 75 per cent nickel and 25 per cent zinc, precipitated by sodium hydroxide from a solution of the corresponding nitrates. The effect of oxidation and reduction of the activator between experiments is likewise shown.

TABLE 78.—*Thermal Decomposition of Alcohol Vapor Using a Nickel-Zinc Catalyst.*

		Composition of Gaseous Products Per Cent by Volume			
Alcohol Vapors Diluted with	Temp., °C.	C_2H_4	H_2	C_2H_6	Rate of Flow cc./min.
- - - -	300	1.2	59.8	11.2	0.23
	Catalyst Oxidized and Reduced				
	375	3.2	50.7	13.6	0.24
	450	3.4	53.0	17.1	0.31
CO_2	350	Nil	12.6	Nil	0.04
	450	Nil	17.9	10.7	0.04
	Catalyst Oxidized and Reduced				
	275	Nil	27.8	Nil	0.05
	300	Nil	29.0	6.3	0.05
H_2O	300	0.4	65.0	6.7	0.35
	500	Nil	44.6	5.9	0.33
	Catalyst Oxidized and Reduced				
	275	0.2	56.5	1.9	0.37

The primary formation of ethane with the nickel-zinc catalyst is indicated by the data in Table 79. The diluents were used to reduce the space velocity of the gases and at the same time decrease the volume of alcohol decomposed. With carbon dioxide present the actual relative yield of ethane was much above that shown by the analyses owing to inclusion of the neutral gas. Any water vapor tends to cut down the quantity of alcohol contacting the catalyst so that the degree of reactivity is lessened. Both of these effects were absent in the case of absolute alcohol.

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[171] C. J. Engelder, *J. Phys. Chem.*, 1917, 21, 676; *Chem. Abs.*, 1918, 12, 13; *J.S.C.I.*, 1918, 37, 19A.

[172] F. Bischoff and H. Adkins, *J.A.C.S.*, 1925, 47, 807; *J.S.C.I.*, 1925, 44, 377B; *Chem. Abs.*, 1925, 19, 1246.

TABLE 79.—*Thermal Decomposition of Alcohol Vapors Diluted with Carbon Dioxide.*

Catalyst Used	Temp., °C.	Composition of Gaseous Products Per Cent by Volume C_2H_4	H_2	C_2H_6	Space Velocity
D	450	2.5	35.6	4.3	50
	450	2.9	35.3	2.7	25
E	350	0.6	14.6	5.5	50
	450	1.8	36.5	9.1	30
	450	2.6	33.3	2.3	50
F	350	0.2	2.3	3.0	25
	450	1.6	27.4	8.7	25
G	450	1.0	36.1	8.6	25
	450	0.4	11.0	2.4	100
H	450	0.6	25.6	7.7	25

Catalysts:

(D), an equimolecular mixture of zinc oxide and chromic oxide triturated in water and dried at 110°C.

(E), copper and chromium with the addition of nickel were precipitated on silica gel.

(F), 10 moles of magnesium to 1 of chromium were precipitated from a solution of their nitrates by the use of ammonium hydroxide.

(G), 1 mole of cupric hydroxide was precipitated from cupric chloride solution by sodium hydroxide. One-tenth mole of manganese dioxide was added as a promoter.

(H), cupric hydroxide, made as above, with incorporation of one-twentieth mole each of titanic acid and molybdic acid as promoters.

The investigators consider the above results as definitely pointing to ethane formation by hydrogenation of ethylene. The temperature effect is noticeable on comparison of data for catalysts (E) and (F). Influence of space velocity may be seen by comparing the data obtained with catalysts (E) and (G), viz., the higher the velocity, the lower the ethane content because of the shorter time the gases are in contact with the catalyst.

Formation of Carbon Dioxide. This took place several times under conditions considered to preclude the decomposition of carbon monoxide as a secondary reaction product. Sometimes gases made up largely of hydrogen and carbon dioxide were obtained accompanied by an oily condensate; at other times the same gaseous mixture occurred without oily condensates.

Lazier and Adkins[173] have suggested formation of ketene, as a secondary reaction, from the aldehyde primary decomposition of ethanol when a dehydrogenating catalyst is employed. Combination of ketene with aldehyde would give carbon dioxide, leaving an unsaturated hydrocarbon. The latter, on polymerizing, could furnish the resin obtained in certain pyrolyses of ethyl alcohol. These possibilities are evident from the reactions,

$$CH_3CHO \longrightarrow H_2 + CH_2{=}CO$$
$$CH_2CO + CH_3CHO \longrightarrow CO_2 + CH_2{=}CHCH_3$$

Boomer and Morris have identified two types of oils from their condensates. One, a pure hydrocarbon of high molecular weight and empirical formula, C_2H_4, was considered as a possible result by way of ketene formation or by ethylene polymerization. Catalyst (F) produced this type of polymer (see Table 80).

The other oil identified in these pyrolysis experiments had an empirical formula, C_5H_8O, and appeared to be a polymer. This oil, when tested for its molecular weight by the cryoscopic method with benzene as solvent, yielded a value of 240, corresponding to a trimer, i.e., $(C_5H_8O)_3$. It was secured after pyrolyzing alcohol and water mixtures, whereas the hydrocarbon oil resulted from treatment of absolute alcohol.

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[173] W. A. Lazier and H. Adkins, *J. Phys. Chem.*, 1920, 30, 895; *Chem. Abs.*, 1926, 20, 2975; *Brit. Chem. Abs.* A, 1926, 918.

TABLE 80.—*Composition of Gases from Thermal Decomposition of Alcohol When Oily Condensates Were Formed.*

Catalyst No.	Temp., °C.	Composition of Gaseous Products Per Cent by Volume				
		CO_2	C_2H_4	H_2	CO	CH_4
A	400	9.2	2.3	88.6	Nil	Nil
	450	8.7	4.9	85.5	Nil	1.0
	500	14.7	3.8	77.8	Nil	3.6
E	450	8.3	3.5	89.2	Nil	Nil
	500	10.6	3.5	86.0	Nil	Nil
C	350	7.3	1.6	91.0	Nil	Nil
	400	18.5	2.8	78.5	Nil	Nil
	450	18.9	3.1	76.8	0.7	0.7
	500	18.9	4.3	76.7	Nil	Nil
F	450	4.8	14.0	80.9	Nil	Nil
	500	10.4	12.7	71.3	2 6	2.9

Catalysts:
(A) and (C) were those employed in experiments given in Table 77.
(E) and (F) were described in Table 79.

In the analyses of the gaseous products in these cases (see Table 81), the relatively low yields of carbon monoxide and methane were considered the result of slight secondary decomposition by the primary acetaldehyde product. The high percentages of hydrogen, indicating excessive dehydrogenation, have led Boomer and Morris to explain formation of these oils as resulting from decomposition of ketene into carbon dioxide and allene, i.e.,

$$2H_2C{=}CO \longrightarrow CO_2 + H_2C{=}C{=}CH_2$$

The latter is known to be very reactive chemically, so that condensations might be expected: for example,

$$H_2C{=}C{=}CH_2 + H_2O = (CH_3)_2CO$$

The resultant compound, acetone, is known to condense when certain catalysts are used. Similarly, the investigators point out that an addition reaction between allene and acetaldehyde could lead to a product of formula $(C_5H_8O)_x$.

TABLE 81.—*Composition of Gases from Thermal Decomposition of Absolute Alcohol When No Oily Condensates Were Formed.*

Catalyst	Temp., °C.	Composition of Gaseous Products Per Cent by Volume				
		CO_2	C_2H_4	H_2	CO	CH_4
J	350	5.6	6.7	76.3	3.3	8.1
	450	17.3	2.4	77.7	1.3	1.1
K	350	5.3	4.0	88.6	Nil	2.1
	450	12.9	6.4	79.6	Nil	1.1
L	350	7.3	1.4	83.3	Nil	8.0
	450	18.1	2.5	77.7	Nil	1.6
M	350	6.8	3.0	88.1	0.2	1.9
	450	18.1	3.0	78.6	Nil	Nil

Catalysts:
(J), normal zinc chromate, precipitated from zinc nitrate solution by potassium dichromate.
(K), 5 moles of zinc hydroxide and 1 mole of chromic hydroxide precipitated from the nitrates by potassium hydroxide.
(L), contained iron, copper, manganese, phosphorus and potassium.
(M), was composed of iron, copper, manganese, boron and potassium. Both L and M were prepared by the method of Audibert and Raineau.[174]

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[174] E. Audibert and A. Raineau, *Rev. ind. min.*, **1928**, No. 182, 286; *Ind. Eng. Chem.*, **1929**, **21**, 880; *Brit. Chem. Abs.* **B**, 1929, 840; *Chem. Abs.*, 1929, **23**, 2094, 5091.

A third type of reaction took place on use of catalysts (J), (K), (L) and (M) with absolute alcohol vapor. Here the liquid products contained no high-boiling fractions and carbon was not deposited in appreciable amounts on the catalysts. This absence of carbon and the small yields of methane and carbon monoxide compared with the production of carbon dioxide led the workers to suggest the following successive hydration reactions to account for carbon dioxide and hydrogen formation:

$$C_2H_5OH + H_2O = 2CH_3OH$$
$$CH_3OH + H_2O = CO_2 + 3H_2$$

It was noted, however, that (1) no methyl alcohol was found among the reaction products; (2) the first reaction has not been shown to occur, although methyl ether (isomeric with ethanol) has been thus hydrated; (3) the second reaction may take place in two stages, with intermediate formation of carbon monoxide, although this oxide was found in such small amounts as to render the occurrence of any such action somewhat improbable.

ALCOHOL AS SOLVENT

New uses for ethyl alcohol as a solvent are being found constantly. Hubert and Lambert[175] add ethyl alcohol or gasoline-alcohol mixtures to bituminous coatings, such as asphalt, bitumen, petroleum or coal distillates. It is reported that the covering materials are thus rendered more adherent to dry or wet surfaces.

Klein[176] extracts oil and coloring substances from wax by a composite solvent made by mixing a formate of a lower aliphatic alcohol and another organic material in which asphaltic substances are more soluble than in the formate.

In a method for refining montan wax,[177] after the crude material has been saponified, alcohol, or an alcohol-acetone mixture, is used to dissolve higher alcohols and soaps from the saponified product. The asphaltic constituents are unaffected by the ethanol solvent.

Ethyl esters having a boiling point between 85 and 158°C., such as ethyl isovalerate, propionate and butyrate, serve as diluents[178] when lubricating oils are dewaxed by chilling processes.

ANALYTICAL REACTIONS FOR ETHYL ALCOHOL

Binary mixtures of ethyl alcohol and water are readily estimated by density determinations, or, in very dilute aqueous solution, by chromic acid oxidation.

Estimation of ethanol in dilute aqueous solution is carried out by Vansheidt and Eremeeva[179] in the following manner. The alcohol is converted into ethyl nitrite by treatment with sodium nitrite solution and phosphoric acid. A stream of carbon dioxide-free air, passed through the solution at 35°C., serves to propel the alkyl nitrite fumes through a heated copper spiral in a combustion tube where they are partly burned. Any unburned fumes are oxidized at 135-140°C. in successive concentrated sulphuric acid solutions of silver dichromate and potassium dichromate, so that the original nitrite is entirely converted into carbon dioxide. The latter is absorbed in 50 per cent caustic potash solution, the gain in weight representing the carbon dioxide equivalent of the alcohol in the sample. Although small amounts of acetaldehyde are reported unobjectionable, it is stated that any ether present in the sample should be removed by aeration before the analysis is attempted.

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[175] O. A. Hubert and P. Lambert, French P. 782,876, 1935; *Chem. Abs.*, 1935, **29**, 7068.

[176] H. Klein, U. S. P. 1,936,453, Nov. 21, 1933; *J. Inst. Pet. Tech.*, 1934, **20**, 41A.

[177] M. Jahrstorfer and E. Walz, German P. 587,450, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1510.

[178] British P. 437,486, 1934, to Sinclair Refining Co.; *Brit. Chem. Abs.* **B**, 1936, 86; *Chem. Abs.*, 1936, **30**, 2365. Also E. C. Herthel, U. S. P. 2,056,723, Oct. 6, 1936, to Sinclair Refining Co., *Chem. Abs.*, 1936, **30**, 8595.

[179] A. Vansheidt and O. Eremeeva, *J. Gen. Chem. (U.S.S.R.)*, 1932, **2**, 800; *Brit. Chem. Abs.* **A**, 1933, 372; *Chem. Abs.*, 1933, **27**, 2651.

Most of the analytical reagents employed in the examination of technical ethyl alcohol are specifically designed for the detection, or estimation, of small amounts of various impurities, including benzene, methyl alcohol and acetaldehyde.

For detecting traces of benzene (1 vol. in 10,000) in alcohol, Lansing[180] recommends dilution with aqueous sodium sulphate and extraction with carbon tetrachloride. The extract is treated with nitrating acid, the carbon tetrachloride is subsequently evaporated, and caustic soda solution and acetone are added to the residue. A red color (with purple tinge) in the top layer indicates benzene. Similarly, toluene gives a slightly brownish yellow and xylene a definite, but not intense, green.

Differences in density and oxidation behavior serve as the basis of a method, reported by Maricq,[181] for estimating mixtures of ethyl and methyl alcohols.

Brown[182] has described a color reaction with vanillin for the detection and approximate estimation of methyl, isopropyl and amyl alcohols in ethyl alcohol.

A method for the identification and estimation of ethyl alcohol in a mixture of organic materials containing higher alcohols has been elaborated by Nicloux.[183]

For the estimation of alcohol in small quantities of biological fluids, Webb[184] reports a modification of Agulhon's[185] reaction. The accuracy of the determination is said to be within 2 per cent of the actual amount present.

A method applicable to the determination of the alcohol content of physiological fluids and tissues as well as biological culture media has been developed by Friedmann and Klaas.[186]

A procedure for analyzing hydrocarbon-containing alcohols, as employed by the Customs Laboratory of Ottawa, is described by Hoff.[187] For the same purpose Bonnier and Juge-Boirard[188] employ a physical method of analysis based on water-tolerance determinations at different temperatures.

Recovery of alcohol used in the estimation of acidity in dark and bright petroleum distillates has been carried out by Ter-Akopova.[189] A system of rectification rendered the alcohol fraction boiling at 78.3°C. and the alcohol-benzene fraction collected at 68-78°C. available as solvents in making further tests; the former for acidity in dark petroleum, the latter for the same determination in bright petroleum products.

Tests of Absolute Alcohol. Absolute alcohol produced by azeotropic methods frequently contains traces of benzene as well as water. For the estimation of these small amounts of impurities, Swietoslawski and Szmigielska[190] have developed a method based on the following facts: (1) the boiling point of the binary alcohol-benzene azeotrope is appreciably lowered by small amounts of water; (2) benzene in small amounts also changes the boiling point of the alcohol-water azeotrope.

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[180] A. C. Lansing, *Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 184; *Brit. Chem. Abs.* B, 1935, 617; *Chem. Abs.*, 1935, **29**, 4696.

[181] L. Maricq. *Ann. brass. distill.*, 1931, **29**, 362; *Chem. Abs.*, 1931, **25**, 5642; *Brit. Chem. Abs.* B, 1931, 874.

[182] C. L. M. Brown, *Pharm. J.*, 1934, **133**, 560; *Chem. Abs.*, 1935, **29**, 2111; *Brit. Chem. Abs.* B, 1935, 137.

[183] M. Nicloux, *Compt. rend.*, 1936, **203**, 16; *Brit. Chem. Abs.* A, 1936, 1229; *Chem. Abs.*, 1936, **30**, 6308.

[184] D. A. Webb, *Sci. Proc. Roy. Dublin Soc.*, 1936, 21, 281; *Brit. Chem. Abs.* A, 1936, 1091.

[185] H. Agulhon, *Bull. soc. chim.*, 1911, (4) **9**, 881; *J.C.S.*, 1911, **100** (2), 1140.

[186] T. E. Friedmann and R. Klaas. *J. Biol. Chem.*, 1936, **115**, 47; *Chem. Abs.*, 1936, **30**, 7136; *Brit. Chem. Abs.* A, 1936, 1229.

[187] R. W. Hoff, *Analyst*, 1934, **59**, 687; *Chem. Abs.*, 1935, **29**, 287; *Brit. Chem. Abs.* B, 1935, 12.

[188] C. Bonnier and M. G. Juge-Boirard, *Ann. combustibles liquides*, 1932, 7, 799; *Brit. Chem. Abs.* B, 1933, 659; *Chem. Abs.*, 1933, **27**, 1135.

[189] M. A. Ter-Akopova, *Novosti, Neft.*, 1936, **3**, No. 13, 6; *Chem. Abs.*, 1936, **30**, 6927.

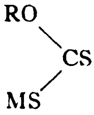
[190] W. Swietoslawski and J. Szmigielska, *Bull. intern. Acad. poloniase Sci.*, 1932, 7, 80; *Chem. Zentr.*, 1933, 1, 814; *Chem. Abs.*, 1933, **27**, 3683; *Brit. Chem. Abs.* B, 1932, 94.

When treated with pulverized potassium hydroxide and carbon disulphide, ethyl alcohol yields potassium ethyl xanthate, mp. 215.3°C., which can be quantitatively titrated with iodine. Other alcohols give analogous xanthates.[191]

The direct titration of xanthate solutions with iodine is based upon the reaction,

$$I_2 + 2C_2H_5O\cdot CS\cdot S^- = 2I^- + (C_2H_5O\cdot CS\cdot S)_2$$

i.e., 2 moles of xanthate are equivalent to 1 mole of iodine. The general formula for a xanthate is



where *R* represents an alkyl radical and *M* an alkali metal. It is obvious that in the quantitative estimation of a xanthate, the amount of standardized reagent used per gram of xanthate depends upon the molecular weight of *R*. Hence, the investigators were able to assign to each alcohol an "alkali reagent number," which sharply characterizes the alcohol. This number for ethyl alcohol is 793 (calculated).

Isomeric alcohols have the same xanthate iodine equivalent, in which case a comparison of the melting points becomes necessary.

The alkali xanthates form in the presence of water so that the alcohol to be tested need not be anhydrous. The method may also be applied directly to a solvent mixture, provided only one alcohol is present.

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[191] W. F. Whitmore and E. Lieber, *Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 127; *Brit. Chem. Abs.* B, 1935, 486; *Chem. Abs.*, 1935, 29, 2878.

Chapter 14

Reaction between Sulphuric Acid and Propene. Production of Isopropyl Alcohol

The commercial manufacture of isopropyl alcohol from propene in cracking gas was initiated in 1919-1920[1] employing the process of Ellis and his associates.[2] Later, this alcohol was produced on a small scale[3] at Okmulgee, Oklahoma. In 1925-1926 isopropyl and other secondary alcohols were made for a short time[4] at Tiverton, Rhode Island, and afterwards at Barnsdall, Oklahoma. These plants continued in operation until 1932, when the manufacturing interests were merged. Isopropyl alcohol (as well as other secondary and tertiary alcohols) is being prepared in large quantities at Bayway, New Jersey.[5] Propene employed for this purpose should be free from higher olefins and also sulphur compounds, although paraffin hydrocarbons do not interfere except as diluents. Originally, gases containing both ethylene and propene were employed, the latter being selectively absorbed in diluted sulphuric acid of controlled concentration. At the present time, however, a propene-propane fraction (substantially free from butenes) is employed. This mixture is obtained as an overhead gas in stabilizer operation.

REACTION BETWEEN SULPHURIC ACID AND PROPENE

When propene is contacted with 90 per cent sulphuric acid at room temperature, or with more concentrated acid at lower temperatures, the main reaction products are the mono- and di-isopropyl esters of the acid: viz. $(CH_3)_2CHSO_4H$ and $[(CH_3)_2CH]_2SO_4$, respectively.[6] It has been shown[7] that the corresponding *n*-propyl derivatives are not formed even in the presence of peroxides. Since the latter had been reported to have a directive effect on the addition of hydrobromic acid to certain unsaturated hydrocarbons[8] it was considered probable that at least partial conversion to *n*-propyl sulphates might take place when peroxides were included in sulphuric acid treatment of the olefin.

The alcohol prepared from the above isopropyl esters, by hydrolysis and subsequent distillation, is accompanied by a small proportion (less than 0.2 per cent) of 4-methylpentanol-2, $(CH_3)_2CHCH_2CHOHCH_3$. The latter compound evidently results from the hydration of 4-methylpentene-2, $(CH_3)_2CHCH_2CH{=}CH_2$, produced by dimerization of propene. Such polymerization should be avoided, as it not only leads to loss of raw material, but often necessitates separation and disposal of undesirable oily substances.

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[1] By the Standard Oil Co. of N. J.

[2] See. Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York. 1934.

[3] By the Doherty Research Co. at the plant of the Empire Refineries.

[4] By the Petroleum Chemical Corp.

[5] By the Standard Alcohol Co.

[6] Earlier work on this reaction and its industrial applications are discussed by Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., 1934.

[7] B. T. Brooks, *J.A.C.S.*, 1934, 56, 1998; *Brit. Chem. Abs.* A, 1934, 1198; *Chem. Abs.*, 1934, 28, 6697.

[8] For the effect of peroxides on the addition of halogen acids to olefins, see Chapter 12.

Since the rate of propene absorption in dilute sulphuric acid does not fall off rapidly with increasing reaction,[9] Brooks[10] suggests the following interactions as taking place in the acid liquor:

(a) monoalkyl esters are first formed as monohydrates of sulphuric acid;

(b) dialkyl esters result from the elimination of water when one mole of hydrate further combines with one mole of olefin.

Production of isopropyl esters, according to this view, is indicated by the equations:

$$C_3H_6 + H_2SO_4 \cdot H_2O \longrightarrow C_3H_7SO_4H \cdot H_2O$$
$$C_3H_7SO_4H \cdot H_2O + C_3H_6 \longrightarrow (C_3H_7)_2SO_4 + H_2O$$

The preparation of isopropyl alcohol from propene involves two separate operations: (1) absorption of the olefin in diluted acid to yield an acid liquor containing isopropyl sulphates, and (2) dilution of the latter with water to effect hydrolysis of the esters, followed by distillation to recover the alcohol.

Absorption of Propene in Sulphuric Acid. The velocity of gaseous propene absorption at 15°C. in sulphuric acid of concentrations varying from 75 to 88 per cent has been studied by Pigulevskii and Rudakova.[11] They found combination to proceed in accordance with the law of unimolecular reactions. The quantity of olefin taken up by unit surface in unit time was proportional to its partial pressure and independent of its concentration, as was also true with ethylene.[12] Furthermore, absorption of propene was found to be autocatalytic. It was also noted that the rate of solution was increased by the presence of silver salts, but much less so by those of vanadium, uranium and tungsten. All of these inorganic compounds exerted less catalytic effect with propene than with ethylene or the butenes. Remiz[13] also reports that a small proportion (3 per cent) of argentic compounds are helpful. However, he employs higher temperatures (110°C.) and more dilute acid (54 per cent). The yield of alcohol is said to be 21 per cent.

The influence of a number of inorganic substances, as well as organic diluents, on the velocity at which unsaturated hydrocarbons are dissolved in sulphuric acid has been investigated by Markovich, Moor and Dement'eva.[14] They likewise observed that salts of silver were the most effective catalysts, and in some instances other compounds exerted an inhibitory action. The organic liquids which were soluble in the acid were practically ineffective except acetone and propionic acid. The presence of acid-insoluble liquids greatly accelerated solution of the gaseous olefins, but chemical interaction took place only when emulsions were formed.

In the commercial production of isopropyl alcohol, sulphation may be accomplished by contacting the olefinic gases with relatively concentrated acid or by treating propene (or propene fractions) under sufficient pressure to maintain liquid-phase conditions. In carrying out gas-phase reaction at low working pressures, the use of an absorbent mineral oil, as proposed by Lebo,[15] greatly increases the capacity of the operating system. In a typical process of this kind, a gas containing 16 to 18 per cent of propene is treated with sulphuric acid and an absorbent oil in a steel tower provided with cooling coils. Interaction is normally prolonged until the liquor contains a substantial proportion of diisopropyl sulphate.[16]

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[9] Considered an indication that there is no increase in the proportion of water to uncombined acid.

[10] B. T. Brooks, *Ind. Eng. Chem.*, 1935, **27**, 278; *J. Inst. Pet. Tech.*, 1935, **21**, 226A; *Chem. Abs.*, 1935, **29**, 2700; *Brit. Chem. Abs.* **B**, 1935, 536. *Proc. World Petroleum Congr.*, 1933, **2**, 840; *Brit. Chem. Abs.* **B**, 1934, 742; *Chem. Abs.*, 1934 **28**, 4871.

[11] V. Pigulevskii and N. Rudakova, *Materials on Cracking Goskhimtekhizdat* (*Leningrad*), **1933**, No. 1, 67; *Chem. Abs.*, 1935, **29**, 2059; *Brit. Chem. Abs.* **A**, 1935, 1082; *J. Inst. Pet. Tech.*, 1935, **21**, 452A. See also, V. Pigulevskii, *Trans. VI Mendeleev Congr. Theoret. Applied Chem. 1932*, 1935, **2**, Pt. 1, 711; *Chem. Abs.*, 1936, **30**, 2734.

[12] See Chapter 13.

[13] E. K. Remiz, *J. Appl. Chem.* (*U.S.S.R.*), 1936, **9**, 703; *Chem. Abs.*, 1936, **30**, 7536; *Brit. Chem. Abs.* **A**, 1936, 819.

[14] M. B. Markovich, V. G. Moor and M. I. Dement'eva, *Materials on Cracking, Goskhimtekhizdat* (*Leningrad*), **1933**, No. 1, *77*; *Chem. Abs.*, 1935, **29**, 2059; *Brit. Chem. Abs.* **A**, 1935, 1085.

[15] R. B. Lebo, U. S. P. 1,865,024, June 28 1932, to Standard Oil Development Co.; *Chem. Abs.*, 1932, **26**, 4344; *Brit. Chem. Abs.* **B**, 1933, 371. See also M. D. Mann, Jr., and R. R. Williams,

Effect of Catalysts. It is stated by van Peski[17] that combination of propene with acid, e.g., 90 per cent sulphuric, may be effected without polymer formation. This he seeks to accomplish by having present in the liquid medium cuprous cyanide or complex copper salts, for example those formed by reaction of cuprous oxide and carbon monoxide or nitric oxide. Catalysts, such as platinum deposited on carbon black or sulphuric acid-soluble salts of iron, nickel, cobalt or silver, are also mentioned for the same purpose and as stabilizers of acid liquors containing isopropyl sulphates.[18] They are reported, too, of assistance in the absorption of propene.[19] Cyanides of iron, nickel or cobalt are likewise suggested for catalyzing the production of olefin sulphates.[20]

According to Dreyfus,[21] propene is absorbed by 90 per cent sulphuric acid which contains 5 per cent of a sulphonic acid or an organic ester of an inorganic acid.[22] Addition of contact agents such as metallic silver or copper was found beneficial; sulphates of calcium, lead, silver, iron or mercury were also used. Among the organic esters recommended were the monosulphuric acid ester of glycol, sulphuric esters of glycerol, hydroxystearo-sulphuric acid, sulphoricinoleic acid, sulphoaromatic stearic acids, and phosphoric esters of glycol or glycerol. Sulphuric acid, he reports, may be substituted by phosphoric acid.

Effect of Rapid Agitation. A special mixer equipped with paddles and rotated at 600 to 1000 r.p.m. was constructed by Dakin and Gutuirya[23] for atomizing acid employed in the extraction of olefins from cracking gases. Working at atmospheric pressure with 90 per cent acid (which selectively removed only propene) 4 to 4.2 kilograms were used for each kilogram of isopropyl alcohol produced. In tests with ethylene, the application of pressures up to 15 atmospheres was found to lower acid consumption by one-third per unit of alcohol obtained.

Effect of Pressure. By utilizing acids weaker than sulphuric, e.g., phosphoric or organic sulphonic acids, Dreyfus[24] prepared isopropyl alcohol (and ether) from propene at high temperatures and pressures. Contact substances, such as metallic silver, silver sulphate, cuprous oxide, and the sulphates of calcium, iron, lead or mercury were found active. Pressures of 30 to 200 atmospheres and temperatures of 150° to 300°C. were required when the concentration of the absorbing liquid was 40 to 75 per cent. Moisture for hydrolyzing the resultant esters was introduced in vapor form.

U. S. P. 1,365,043, Jan. 11, 1921, to Standard Oil Development Co.; Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., Inc., New York, 1934, 351.

[16] B. T. Brooks, *Ind. Eng. Chem.*, 1935, **27**, 278; *Chem. Abs.*, 1935, **29**, 2700; *Brit. Chem. Abs.* **B**, 1935, 536; *J. Inst. Pet. Tech.*, 1935, **21**, 226A.

[17] A. J. van Peski, U. S. P. 1,995,908, Mar. 26, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 3349. German P. 599,151, 1934 to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 5831.

[18] A. J. van Peski, U. S. P. 2,010,337, Aug. 6, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 6245; *Brit. Chem. Abs.* **B**, 1936, 919.

[19] A. J. van Peski, U. S. P. 1,999,621, Apr. 30, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 4021.

[20] German P. 598,538, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 5831. See also, A. J. van Peski, U. S. P. 1,944,622, Jan. 23, 1934, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 2012.

[21] H. Dreyfus, British P. 409,676, 1934; *Chem. Abs.*, 1934, **28**, 6156; *Brit. Chem. Abs.* **B**, 1934, 617; *J. Inst. Pet. Tech.*, 1934, **20**, 429A. U. S. P. 2,015,105, Sept. 4, 1934; *Chem. Abs.*, 1935, **29**, 7342.

[22] Excluding alkyl hydrogen sulphates.

[23] M. A. Dakin and V. S. Gutuirya, *Azer. Neft. Khoz.*, 1934, No. 2, 90; *Chem. Abs.*, 1934, **28**, 7489; *J. Inst. Pet. Tech.*, 1935, **21**, 418A.

[24] H. Dreyfus, British P. 397,187, 1933; *Chem. Abs.*, 1934, **28**, 777; *Brit. Chem. Abs.* **B**, 1933, 904. French P. 749,951, 1933; *Chem. Abs.*, 1934, **28**, 777.

ACID ABSORPTION OF MIXED OLEFINS

In treating a mixture of unsaturated hydrocarbons for the production of both ethyl and isopropyl alcohols, Dreyfus and Groombridge[25] propose combination of propene selectively with about 87 per cent sulphuric acid at 20° to 23°C. They then esterify the residual olefin (ethylene) with acid of 75 to 85 per cent concentration at 90° to 130°C. According to Groombridge,[26] only the higher olefin is extracted by employing 70 to 90 per cent acid at 15° to 25°C. and a gas pressure of 10 to 30 atmospheres. Addition of water to the acid liquor as esterification proceeds may be utilized to maintain a constant concentration of the acid phase.[27]

In a process disclosed by Merley,[28] cracking gases are passed into concentrated sulphuric acid (*d* 1.84) at −15°C. until the density falls to less than 1.263. The solution thus obtained is further treated, at the same low temperature, with the liquid hydrocarbons produced by cracking. The resultant liquor contains chiefly isopropyl acid sulphate and is free of organic sulphonic acids. After hydrolysis, the recovered acid may be concentrated and reused. A mixture of equal volumes of glacial acetic acid and hydrogen sulphate containing a few per cent of water has been proposed by Woolcock[29] for selective reaction with propene at 40°C. The liquid medium is afterwards heated to secure isopropanol. Some isopropyl acetate is formed simultaneously.

Lacy[30] treats olefinic gases by countercurrent washing with 60 to 87 per cent sulphuric acid at 35° to 65°C. The liquid at the base of the scrubbing tower may be separated from polymers (if present) and recirculated until its effective alcohol concentration is about 40 per cent.

Another procedure,[31] especially applicable for the treatment of cracking gases containing butenes and lower olefins, is as follows: the gases are first subjected to the action of cuprous chloride, dissolved in aqueous ammonium chloride, to eliminate any diolefin (butadiene) without polymerizing it.[32] Tertiary olefins are next removed by 60 to 65 per cent sulphuric acid at 25°C. or lower. Following this, the *n*-butenes are reacted with slightly more concentrated acid (65 to 70 per cent) at somewhat higher temperatures (35° to 60°C.). Residual propene is thereafter absorbed in acid of 80 to 85 per cent strength, but at 20° to 40°C.

CONTINUOUS METHODS FOR HYDRATING PROPENE

An interesting procedure for the preparation of isopropyl alcohol comprises contacting the corresponding olefin, under slight pressure, with relatively dilute sulphuric acid.[33] From time to time, the condition of the reacting liquor was measured (after cooling with ice water) by direct titration, using bromthymol blue as an indicator. At first the acidity diminished, but later (on continued treatment with the olefin) increased, until finally, practically all the acid originally present reappeared in the free state. This phenomenon seemed to indicate direct hydration of the olefin to alcohol as an overall effect. In a process utilizing such conditions, the free alcohol may be extracted with an acid-resistant solvent such as phenol, cresol, anisole or phenetole. The acid solution is then available for reuse after addition of sufficient water to adjust its concentration. The necessity for reconcentrating the absorbing medium is thus eliminated.

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[25] H. Dreyfus and W. H. Groombridge, British P. 403,654, 1933, to British Celanese Ltd.; *Brit. Chem. Abs.* **B**, 1934, 355; *J. Inst. Pet. Tech.*, 1935, **21**, 383A; *Chem. Abs.*, 1934, **28**, 3415.

[26] W. H. Groombridge, British P. 415,766, 1933, to British Celanese Ltd.; *Brit. Chem. Abs.* **B**, 1934, 952; *Chem. Abs.*, 1935, **29**, 811.

[27] See also, H. Dreyfus, French P. 782,487, 1935; *Chem. Abs.*, 1935, **29**, 6901.

[28] S. R. Merley, U. S. P. 1,897,812, Feb. 14, 1933, to Doherty Research Co.; *Brit. Chem. Abs.* **B**, 1933, 955; *Chem. Abs.*, 1933, **27**, 2696.

[29] J. W. Woolcock, U. S. P. 1,938,162, Dec. 5, 1933, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1934, **28**, 1058.

[30] K. B. Lacy, U. S. P. 1,991,948, Feb. 19, 1935, to Van Schaack Bros. Chem. Works, Inc.; *Brit. Chem. Abs.* **B**, 1936, 88; *Chem. Abs.*, 1935, **29**, 2174.

[31] B. T. Brooks, U. S. P. 2,058,851, Oct. 27, 1936, to Standard Alcohol Co.; *Chem. Abs.*, 1937, **31**, 109.

[32] The removal of diolefins from gaseous mixtures is discussed in Chapter 4.

[33] French P. 799,704, 1936, to Usines de Melle (Soc. anon.); *Chem. Abs.*, 1936, **30**, 8240.

Production of isopropyl alcohol by the above method may be carried out under 3 atmospheres pressure. Sulphuric acid, of 75 per cent concentration, containing 0.5 per cent of cuprous oxide, or of lead, bismuth, silver or gold as catalyst, is employed. After absorption is complete, the liquid product is transferred to another vessel for extraction with 3 times its volume of butylcresol. When the latter operation is complete and stratification has occurred, the aqueous layer is withdrawn and returned to the absorption unit of the system. The cresol layer, containing about 50 grams of isopropyl alcohol per liter of solution and a small proportion of acid, is subjected to washing with a small quantity of water. It is then fractionated to furnish a distillate consisting of the binary isopropanol-water azeotrope and a residue of butylcresol. The latter, after cooling and removing any water which separates, is reverted to the extraction unit. This process is illustrated diagrammatically in Fig. 103.

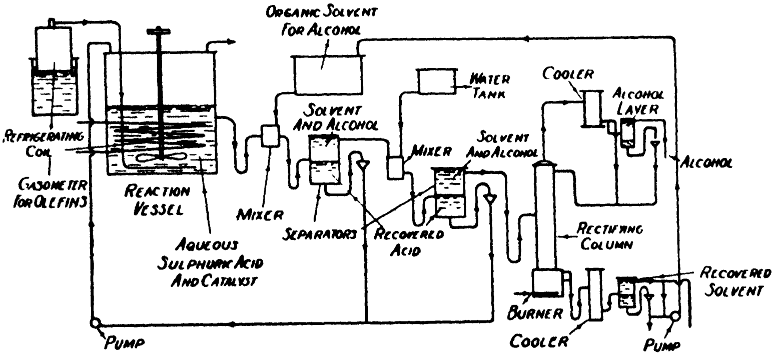

FIG. 103.—Continuous Method for Hydration of Propene to Isopropyl Alcohol. (Usines de Melle, Soc. anon.)

ISOPROPYL ETHER

As previously mentioned, isopropyl ether is sometimes obtained as a by-product in the preparation of isopropyl alcohol. Under appropriate conditions, however, this ether may be the principal substance resulting from the interaction of sulphuric acid and propene. For example, the olefin (under 3 to 7 atmospheres pressure) may be treated in a countercurrent manner in a packed tower with 75 per cent sulphuric acid at 75° to 125°C.[34] Unreacted gaseous paraffins (if present) escape at the top of the tower while at the base is withdrawn the acid solution containing absorbed propene. The liquid medium, after passing through heat exchangers (for preheating fresh acid), is subjected to distillation.

[34] French P. 793,482, 1936, to Standard Alcohol Co.; *Chem. Abs.*, 1936, 30, 4516.

The latter operation yields vapors of isopropyl ether admixed with some propene and isopropanol. These are conducted through a scrubbing tower containing alkali (e.g., sodium carbonate) and thence to a rectifying column, which effects separation into olefin, ether and alcohol. The olefin is returned to the absorption unit, while the alcohol is either withdrawn from the system or is mixed with acid liquor and redistilled. Recovered acid from the last-named step is employed again in the treatment of olefinic gases. A diagrammatic sketch of this process is shown in Fig. 104.

DIISOPROPYL SULPHATE

When propene, under a pressure of several atmospheres, is contacted with sulphuric acid of about 85 per cent strength at 15° to 20°C., the main reaction product is diisopropyl sulphate.[35] Thus, Brooks and Cardarelli[36] accomplish practically complete sulphation of the olefin by treating it under a pressure of 100 lb. per sq. in. with 80 per cent acid at 25°C. The advantage of carrying the reaction to the di-ester stage is that acid consumption per unit of isopropanol produced is thereby reduced and reconcentration costs correspondingly diminish. Moreover, by operating under sufficient pressure, liquid propene (or propene-propane mixtures) may be utilized and interaction prolonged for a considerable period of time in relatively simple equipment.

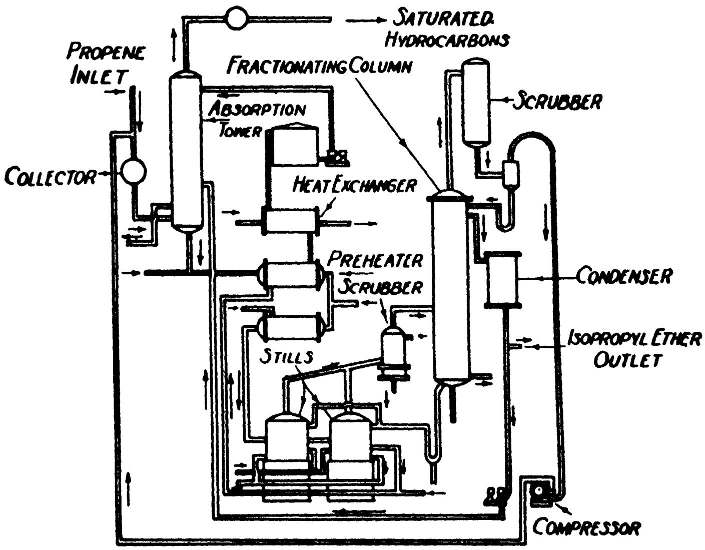

FIG. 104.—Diagrammatic Sketch of Process for Production of Isopropyl Ether. (Standard Alcohol Co.)

Another process comprises combination of the unsaturated hydrocarbon, under

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[35] B. T. Brooks, *Ind. Eng. Chem.*, 1935, **27**, 278; *Brit. Chem. Abs.* **B**, 1935, 536; *Chem. Abs.*, 1935, **29**, 2700; *J. Inst. Pet. Tech.*, 1935, **21**, 226A.

[36] B. T. Brooks and E. J. Cardarelli, U. S. P. 1,919,617, July 25, 1933, to Standard Alcohol Co.; *Brit. Chem. Abs.* **B**, 1934, 442; *Chem. Abs.*, 1933, **27**, 4818.

20 atmospheres pressure, with 90 to 100 per cent acid at 70° to 80°C.[37] The resulting ester may then be separated by distillation under reduced pressures, e.g., not over 20 mm. of mercury. This material is afterwards hydrolyzed and isopropyl alcohol recovered by fractionation. The dilute acid obtained by these steps is described as free from carbonaceous bodies and ready for reconcentration. It is reported that the above procedure avoids ether formation during hydrolysis.

Liquid-Phase Absorption

An apparatus for effecting liquid-phase reaction has been described by Young.[38] He suggests forcing a mixture of liquid propene and 80 to 100 per cent acid through an extended flow-path of constricted cross-section. The operating temperature is kept below 40°C. For example, 93 per cent sulphuric acid and liquid hydrocarbons (containing 95 per cent propene) are conducted through a 35-foot coil of steel tubing (1/8 inch bore and 1/4 inch external diameter) under a pressure of 200-400 lb. per sq. in. The temperature in this instance was maintained between 0° and 5°C. The hourly rates of flow of acid and hydrocarbons were 671 grams and 312 grams, respectively. The products consisted of a gas containing 50 per cent propene and a clear acid liquor containing 28.6 per cent of isopropyl sulphates. Hydrolysis of the latter was accomplished by addition of ice. Distillation yielded over 90 per cent of the reacted olefin in the form of isopropanol.

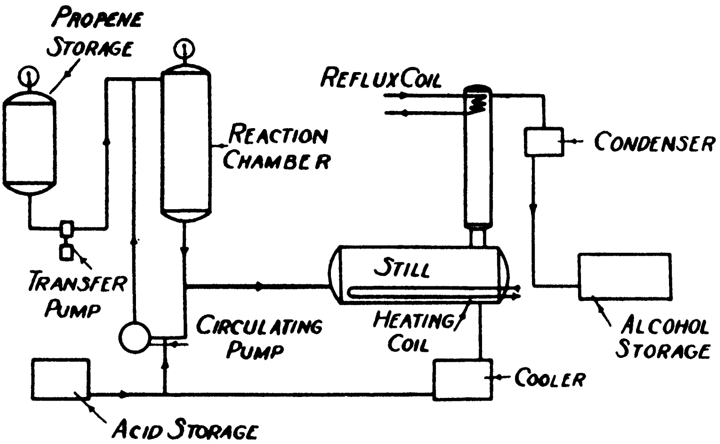

Fig. 105.—Flow Diagram for Liquid-phase Reaction of Propene with Sulphuric Acid. (W. H. Shiffler, M. M. Holm and W. P. Anderson)

Shiffler, Holm and Anderson[39] recommend the use of 50-85 per cent sulphuric acid and temperatures of less than 50°C. The most favorable concentration is 70 per cent by weight. Conversion of the olefin to alcohol may be effected by circulating the liquid reactants under pressure through a lead-lined vessel. For propene-propane mixtures a gage pressure of 125 lb. is sufficient. One type of apparatus which may be employed is illustrated in Fig. 105. The effect of various concentrations of acid on the absorption of the unsaturated hydrocarbon is shown in Table 82.

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[37] British P. 446,614, 1936, to Standard Alcohol Co.; *Brit. Chem. Abs.* B, 1936, 919; *Chem. Abs.*, 1936, 30, 6765; *J. Inst. Pet. Tech.*, 1936, 22, 322A.

[38] H. S. Young, U. S. P. 2,047,606, July 14, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, 30, 6010. British P. 448,457, 1936; *Chem. Abs.*, 1936, 30, 7126; *J. Inst. Pet. Tech.*, 1936, 22, 411A.

[39] W. H. Shiffler, M. M. Holm and W. P. Anderson, U. S. P. 1,988,611, Jan. 22, 1935, to Standard Oil Co. of Calif.; *Brit. Chem. Abs.* B, 1936, 54; *Chem. Abs.*, 1935, 29, 1431.

TABLE 82.—*Effect of Acid Concentration on Propene Absorption from Liquefied Propene-Propane Mixtures. Gage Pressure, 125 lb.*

Sulphuric Acid Used		Liquid Hydrocarbon Mixture			
Gals.	Conc.	Gals.	Propene Content	Period of Reaction	Propene Absorbed
61	73%	77	52.8%	2 hrs.	91%
80	67.8%	100.5	55%	4.5 hrs.	84%
80	65.5%	100.5	55%	5 hrs.	52%

Since the temperature rises somewhat during interaction, provision is made to hold the contact vessel below 50°C. Under these conditions no oily polymers are formed.

After absorption is completed, the acid liquor is withdrawn, diluted with water to about 50 per cent acidity and subjected to steam distillation to recover the alcohol. Reconcentration of the acid to the requisite 70 per cent was effected in the still after removal of isopropanol. In addition to the latter product, some propene (resulting from dehydration of alcohol) and isopropyl ether were obtained. The relative proportions of alcohol and ether depend upon the acid concentration in the distillation unit, stronger acid being conducive to ether formation.

HYDROLYSIS OF ISOPROPYL SULPHATES

As in the case of ethyl esters of sulphuric acid, isopropyl sulphates, although fairly stable in water at ordinary temperatures, are readily hydrolyzed on heating. The rate of hydrolysis is greatly accelerated by the presence of sulphuric, or other, acid. With moderate concentrations the following equilibria are probably set up:

$$C_3H_7SO_4H + H_2O \rightleftharpoons C_3H_7OH + H_2SO_4$$
$$(C_3H_7)_2SO_4 + H_2O \rightleftharpoons C_3H_7SO_4H + C_3H_7OH$$

However, on dilution with the quantity of water usually employed in industrial practice, approximately complete conversion of the esters to the corresponding alcohol is attained. From diisopropyl sulphate, which is generally present in substantial amounts in the liquor from absorption operations, a certain proportion of diisopropyl ether may be produced, according to the equation:

$$(C_3H_7)_2SO_4 + C_3H_7OH \longrightarrow (C_3H_7)_2O + C_3H_7SO_4H$$

Formation of ether may be minimized by removing the dialkyl sulphate and hydrolyzing it separately. In such instances, the concentration of the resultant alcohol should be maintained as low as possible, e.g., by distilling it off as fast as it is formed.[40]

Another by-product of the hydrolysis of isopropyl sulphates in acid solution is propene, probably from dehydration of isopropanol. This side-reaction is almost eliminated by the use of 35 per cent sulphuric acid. An analogous reversion to olefin is more likely to occur in the recovery of higher secondary and tertiary alcohols. It is sometimes found advantageous to carry out hydrolysis for a considerable period prior to distillation,[41] but this does not appear to be the usual practice.

The general procedure employed in the manufacture of isopropyl alcohol, after absorption of the olefin in acid, is as follows: (1) dilution of the reaction mixture with sufficient water to reduce its acidity below 50 per cent (in most instances to about 35 per cent) and (2) immediate distillation to secure a constant-boiling mixture of alcohol and water as an overhead product. Residual acid may then be reconcentrated and employed in the absorption stage.

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[40] B. T. Brooks, *Ind. Eng. Chem.*, 1935, **27**, 278; *Brit. Chem. Abs.* **B**, 1935, 536; *Chem. Abs.*, 1935, **29**, 2700. *Proc. World Petroleum Congr.*, 1933, **2**, 840; *J. Inst. Pet. Tech.*, 1934, **20**, 105A.

[41] W. H. Groombridge and R. J. Peek, British P. 428,792, 1935, to British Celanese Ltd.; *Chem. Abs.*, 1935, **29**, 6901; *Brit. Chem. Abs.* **B**, 1935, 664.

Groombridge and Peek[42] propose to dilute acid liquor with about 5 moles of water to each mole of isopropanol virtually present. The solution is then fed into the top of a copper column packed with pumice and provided with a dephlegmator. The base of the column is heated to 130°C. In this manner the temperature at the top is maintained sufficiently high to effect hydrolysis of the esters and immediate distillation of the resulting alcohol (or ether). Concentration of the acid is said to be effected as it flows downward through the column. Wilson[43] recommends admixing bauxite during interaction of isopropyl sulphates and water, thus forming aluminum sulphate as a by-product. Alternatively, the metallic oxide may be added after hydrolysis and distillation have occurred. In the latter instance if any tarry material is present it should first be removed by heating at 175° to 200°C., so as to avoid contamination of the aluminum salt.

Another method comprises emulsifying acid solutions of dialkyl sulphates, at 70° to 80°C., with an equal weight of water and then distilling[44] the mixture. Higher temperatures may be employed in the first operation provided it is carried out under refluxing conditions.

DEHYDRATION OF ISOPROPYL ALCOHOL

The azeotrope of isopropyl alcohol and water (obtained by fractional distillation at atmospheric pressure) boils at 80.35°C. and contains 12.3 per cent (by weight) of water. Practically anhydrous alcohol can be recovered from this binary mixture by distilling in the presence of water-entraining agents, such as toluene, xylene, ethylene dichloride or benzine fractions.[45] As a method for extracting water from aqueous isopropyl alcohol, van Peski and Smithuysen[46] first carry out an azeotropic distillation of the solution, with benzene, benzine or ethyl chloride as entraining agent. The azeotropic mixture obtained is then extracted with a non-aqueous liquid: for this purpose kerosene, paraffinum liquidum or Edeleanu extract of spindle oil are available.

In other instances, solid drying agents, for example, anhydrous copper sulphate or calcium oxide, may be employed. Brooks[47] recommends contacting the liquid with a concentrated aqueous solution of sodium or potassium hydroxide or of calcium or zinc chloride.

Dehydration by any of these methods is said to be advantageous when followed by a final rectification which effectively separates the alcohol from ill-smelling polymers.[48] Incidentally, the latter compounds may be extracted from acid liquor (before or after hydrolysis) by the same solvents which are applicable in the azeotropic dehydration of isopropanol.[49]

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[42] W. H. Groombridge and R. J. Peek, British P. 428,792, 1935, to British Celanese Ltd.; *Chem. Abs.*, 1935, 29, 6901; *Brit. Chem. Abs.* B, 1935, 664.

[43] W. S. Wilson, U. S. P. 1,931,014, Oct. 17, 1933 to Merrimac Chemical Co.; *Chem. Abs.*, 1934, 28, 173; *Brit. Chem. Abs.* B, 1934, 872.

[44] N. A. Sargent, U. S. P. 2,045,616, June 30. 1936, to Merrimac Chemical Co.; *Chem. Abs.*, 1936, 30, 5591. British P. 427,233, 1935; *Brit. Chem. Abs.* B, 1935, 619; *Chem. Abs.*, 1935, 29, 6245.

[45] For a review of such methods, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[46] A. J. van Peski and W. C. Smithuysen, U. S. P. 2,050,513, Aug. 11, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, 30, 6759.

[47] B. T. Brooks, U. S. P. 2,022,274, Nov. 25, 1935, to Standard Alcohol Co.; *Chem. Abs.*, 1936, 30, 731; *Brit. Chem. Abs.* B, 1936, 1192.

[48] British P. 395,202, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, 28, 172; *Brit. Chem. Abs.* B, 1933, 855.

[49] British P. 411,303, 1933, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* B, 1934, 709.

Anhydrous gypsum, prepared by heating plaster of Paris or gypsum to 160-180°C. has been found effective for the vapor-phase dehydration of aqueous alcohol.[50] The inorganic salt is changed into a hemihydrate which can be subsequently reheated and reused.[51]

REFINING OF ISOPROPANOL

Tertiary butanol is often found as an impurity in isopropyl alcohol made from cracking gases. Its presence, even in relatively minute proportions, can be readily detected by heating the specimen (under examination) with a sulphuric acid solution of mercuric sulphate for 20 to 30 minutes on a water bath. The formation of a yellow precipitate (or discoloration) is characteristic of tertiary alcohols.[52]

For the removal of tertiary butanol (and other analogous alcohols) from secondary alcohols, advantage may be taken of the ease of anhydration of the former under the influence of dilute acids. Thus, Buc[53] suggests heating crude isopropyl alcohol with concentrated sulphuric acid (sp. gr. 1.84) that has been diluted with an equal volume of water. For example, 200 cc. of diluted acid are added to 1000 cc. of alcohol and the mixture heated to boiling temperature, under reflux on a water bath, for about 48 hours. The product will be found to contain only traces of tertiary impurities, say about 0.05 per cent, in a material carrying 3 per cent originally. For a higher degree of purity the heating may be continued 24 hours longer.

During the purification, some isopropanol, up to 10 per cent, may be lost by conversion to propene. It is recommended that the concentration of the acid be reduced by the addition of more water, before separating the refined product by fractional distillation of the acid liquor. The treatment may be carried out more rapidly with acid of higher concentration, but the losses of isopropanol will be greater and a certain amount of polymerization may be expected. A similar purification, recommended by Lebo,[54] comprises warming the alcoholic mixture (at temperatures not above 40°C.) with 20 per cent sulphuric acid and a compound of vanadium, aluminum or copper. Olefinic hydrocarbons produced during this operation are continuously recovered. They may be converted again into tertiary alcohols by absorption in sulphuric acid followed by hydrolysis and distillation.

Merley[55] suggests passing alcohol vapors, at 95° to 97°C., countercurrent to a stream of dilute sulphuric acid (about 25 per cent concentration) to effect elimination of easily decomposable alcohols and also of sulphur compounds. Another procedure for removal of the latter comprises treatment with an aqueous solution of sodium plumbite.[56] Afterwards the alcohol is subjected to rectification and fractionation.

Technical isopropanol may sometimes contain a small proportion of oily polymers which cause a turbidity on dilution with water. The cloudiness is first noticeable with 0.6 per cent of the latter liquid. Refining may be accomplished, according to Rudakova,[57] by treating with petroleum ether, calcium hydroxide, and sodium chloride, followed by filtration through charcoal.

[50] See Chapter 13 for a discussion of the Gyp process for dehydrating alcohols.

[51] British P. 394,086, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 172; *Brit. Chem. Abs.* **B**, 1933, 822.

[52] G. Denigès, *Compt. rend.*, 1898, **126**, 1147, 1277; *J.S.C.I.*, 1898, **17**, 693, 697; *J.C.S.*, 1898, **74** (1), 546, 618.

[53] H. E. Buc, U. S. P. 1,911,798, May 30, 1933, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1934, 186; *Chem. Abs.*, 1933, **27**, 3943.

[54] R. B. Lebo, U. S. P. 1,949,211, Feb. 27, 1934, to Standard Alcohol Co.; *Brit. Chem. Abs.* **B**, 1935, 13; *Chem. Abs.*, 1934, **28**, 2724.

[55] S. R. Merley, U. S. P. 1,933,505, Oct. 31, 1933, to Doherty Research Co.; *Chem. Abs.*, 1934, **28**, 493; *Brit. Chem. Abs.* **B**, 1934, 872.

[56] F. M. Archibald and C. M. Beamer, U. S. P. 1,995,597, Mar. 26, 1935, to Standard Alcohol Co.; *Chem. Abs.*, 1935, **29**, 2973.

[57] N. V. Rudakova, *Materials on Cracking, Khimteoret (Leningrad)*, 1935, No. 2, 192; *Chem. Abs.*, 1935, **29**, 6033; *Brit. Chem. Abs.* **B**, 1936, 631.

Chapter 15

Properties and Uses of Isopropyl Alcohol and Its Derivatives

Details of the preparation of isopropyl alcohol from propene by the sulphation process have been given in the previous chapter. Separation of the resulting alcohol from impurities, such as tertiary butyl alcohol and oily polymers, was also discussed. The following account of the properties of pure isopropyl alcohol and of its numerous applications in industrial and scientific work is intended to supplement that already provided in the previous volume.[1]

PHYSICAL PROPERTIES OF ISOPROPYL ALCOHOL

Some data relating to various physical constants of pure anhydrous isopropyl alcohol are summarized in Table 83.

TABLE 83.—*Physical Properties and Constants of Isopropyl Alcohol.*[2]

Melting point	-85.8°C.
Boiling point	82.4°C. at 760 mm.; $dt/dp = 0.033$°C. per mm.
Vapor pressure	32.4 mm. of Hg. at 20°C.
Density	$d_4^{20} = 0.7887$ (0.7283 at boiling point)
Flash point (closed cup)	11.7°C. or 53°F.
Refractive index (n_D)	1.37925 at 15°C.; 1.37757 at 20°C., 1.3749 at 25°C.
Critical temperature	234.9°C.
Critical pressure	53 atmospheres.
Latent heat of vaporization (at 82.4°C.)	160 cal. per gm.
Heat of combustion	7970 cal. per gm.; 474.8 kg.-cal. per mole
Sheafer heat (cal. per gm. per °C.)	0.563 at 0°C.; 0.677 at 30°C.; 0.740 at 50°C.
Surface tension	21.7 dynes per cm. at 20°C.
Dielectric constant	26 at 20°C.
Electrical conductivity	35×10^{-7} reciprocal ohms at 25°C.
Heat of fusion	21.08 cal. per gm. at melting point.
Vapor density	2.127 at 100°C.
Heat conductivity	3.683×10^{-4} c.g.s. units at 0°C.

The variation of surface tension of isopropyl alcohol against its vapor (mixed with air) is shown in Table 84.[2a]

TABLE 84.—*Surface Tension of Isopropyl Alcohol Against Its Vapor.*

Temp., °C.	Surface Tensions (dynes per cm.)
5	22.8
20	21.7
50	19.3
80	17.0

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[1] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[2] B. T. Brooks, *Chem. Industries*, 1933, **33**, 331; *Chem. Abs.*, 1934, **28**, 4871. *World Petroleum Congr., London*, 1933, *Proc.* **2**, 840; *Chem. Abs.*, 1934, **28**, 4871; *Brit. Chem. Abs.* B, 1934, 742.

[2a] "International Critical Tables," McGraw-Hill Book Co., New York, 1929, Vol. **4**, p. 450.

The following properties of the pure alcohol have also been determined, namely: electric absorption,[3] absorption coefficients for homogeneous X-rays,[4] anomalous dispersion and absorption of electric waves,[5] infra-red absorption,[6] magnetic susceptibilities,[7] thermal conductivity under high pressure,[8] and magneto-optical dispersion in the ultraviolet region.[9] The dielectric constant and molecular polarization of isopropyl alcohol vapor at —80°C. have been measured by Kubo.[10] Data for the scattering of light by the vapor of this alcohol are available from the work of Rao.[11]

TABLE 85.—*Freezing Points of Isopropyl Alcohol-Water Mixtures.*[12]

Per Cent by Volume of Isopropyl Alcohol	Freezing Point °C.	°F.
10	− 2	28
20	− 5	23
30	− 8	17
40	−14	+ 7
50	−22	− 8
60	−32	−26
91 thick syrup at	−50	
cloudy at	−53	
mush at	−56	

TABLE 86.—*Surface Tension of Isopropyl Alcohol-Water Mixtures at 15°C.*[13]

Moles of Isopropyl Alcohol per Liter	Dynes per cm.
1.0	46.58
0.5	53.66
0.25	60.37
0.125	65.21
0.625	68.56
0.0313	70.77

TABLE 87.—*Specific Heats and Densities of Some Isopropyl Alcohol-Water Mixtures.*[14]

Isopropyl Alcohol Per Cent by Weight	d_{15}^{15}	Specific Heat (18°-100°C.), cal. per gm.
100.00	0.78982	0.7233
89.66	0.81770	0.7749
80.01	0.84050	0.8184
70.08	0.86402	0.8695
59.94	0.88782	0.9189
49.97	0.91130	0.9594
39.95	0.93426	0.9996
30.00	0.95576	1.0278
19.99	0.97244	1.0525 (max.)
10.00	0.98448	1.0325

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[3] P. Beaulard, *Compt. rend.*, 1910, 151, 55; *Chem. Abs.*, 1910, 4, 3161; *J.C.S.* 1910, **98** (2), 680.

[4] E. G. Taylor, *Phys. Rev.* 1922, **20**, 709; *J.C.S.*, 1923, **124** (2), 365; *Chem. Abs.*, 1923, **17**, 684.

[5] S. Mizushima, *Bull. Soc. Chem. Japan*, 1926, 1, 83, 115; *Chem. Abs.*, 1926, **20**, 294; *Brit. Chem. Abs.* **A**, 1926, 778, 886.

[6] E. K. Plyler and T. Burdine, *Phys. Rev.*, 1930, **35**, 605; *Brit. Chem. Abs.* **A**, 1930, 662; *Chem. Abs.*, 1930, **24**, 3437.

[7] S. S. Bhatnagar, R. N. Mathur and R. S. Mal, *Phil. Mag.*, 1930, (7) **10**, 101; *Brit. Chem. Abs.* **A**, 1930, 1096; *Chem. Abs.* 1930, **24**, 5550.

[8] P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1923, **59** (7), 141; *Chem. Abs.*, 1924, **18**, 1227.

[9] C. C. Evans and E. I. Evans, *Phil. Mag.*, 1929 (7), **8**, 131; *Brit. Chem. Abs.* **A**, 1929, 1365; *Chem. Abs.*, 1930, **24**, 3441.

[10] M. Kubo, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1935, **27**, 65; *Chem. Abs.*, 1935, **29**, 6481; *Brit. Chem. Abs.* **A**, 1935, 916.

[11] S. R. Rao, *Indian J. Physics*, 1927, **2**, 61; *Chem. Abs.*, 1928, **22**, 1091; *Brit. Chem. Abs.* **A**, 1927, 1127.

[12] R. B. Lebo, *J.A.C.S.*, 1921, **43**, 1005; *Chem. Abs.*, 1921, **15**, 2576; *J.C.S.*, 1921, **120** (1), 493.

[13] R. B. Lebo, *Loc. cit.*

[14] A. G. Doroshevskii, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 958; *J.C.S.*, 1909, **96** (2), 967; *Chem. Abs.*, 1910, **4**, 1404; *J.S.C.I.*, 1910, **29**, 174.

Physical data for binary mixtures of isopropyl alcohol and water are of considerable industrial importance. Results reported for such combinations appear in Tables 85 to 88.

TABLE 88.—*Refractive Indices and Densities of Isopropyl Alcohol-Water Mixtures.*[15]

Isopropyl Alcohol Per Cent by Weight	N_D^{20}	d_{20}^{20}
2.85	1.3335	0.9962
3.56	1.3340	0.9952
4.95	1.3375	0.9888
10.08	1.3392	0.9866
20.08	1.3478	0.9755
29.83	1.3542	0.9654
40.00	1.3590	0.9520
50.15	1.3632	0.9345
60.10	1.3678	0.9137
69.99	1.3712	0.8900
80.00	1.3745	0.8640
90.01	1.3769	0.8338
94.97	1.3770	0.8160
99.50	1.3775	0.7953

Isopropyl alcohol forms a constant-boiling mixture with water, containing 91.1 per cent by volume of the alcohol (87.7 per cent by weight) and boiling at 80.4°C. under 760 mm. pressure. This binary azeotrope has the following physical constants: d_4^{20}, 0.8158; $d_{60°F}^{80°F}$ 0.8190; N_D^{20} 1.3765; viscosity, 0.02106 poise at 25°C.; closed flash point, 64°F.; and coefficient of expansion, 0.001062 per °C.

The free energy of hydration of a number of alcohols, including isopropyl alcohol, has been calculated by Butler, Ramchandani and Thomson[16] from their experi-

TABLE 89.—*Binary Azeotropic Mixtures of Isopropyl Alcohol with Other Organic Compounds.*

Other Component	% by Weight of Isopropyl Alcohol	Boiling Point, °C./760 mm.
Methyl iodide	3.1	42.3
Carbon bisulphide	0.8	44.6
n-Propyl chloride	3.9	45.8
Chloroform	4.2	60.8
n-Hexane	22.	61.
Isobutyl chloride	17.	63.8
Isopropyl ether	10.	64.9
n-Propyl bromide	16.	65.2
Carbon tetrachloride	18.	67.0
Cyclohexane	33.	68.6
Cyclohexene	36.	71.0
Benzene	33.3	71.9
Ethylene dichloride	45.	74.0
Trichlorethylene	28.	74.
Ethyl acetate	23.	74.8
Acetonitrile	55.	75.
Isobutyl bromide	33.	75.5
Methyl propionate	28.	77.
Methyl ethyl ketone	30.	77.3
Dichlorobromomethane	27.6	78.
Isopropyl acetate	52.3	80.1
Toluene	69.	80.6
Tetrachlorethylene	80.6	81.7
Isobutyl iodide	77.	81.6
Chloropicrin	66.5	82.0

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[15] C. T. Bennett and D. C. Garratt, *Perfum. and Essential Oil Rev.*, 1925, 16, 18; *Chem. Abs.*, 1925, 19, 1125; *Brit. Chem. Abs.* B, 1925, 264.

[16] T. A. V. Butler, C. N. Ramchandani and D. W. Thomson, *J.C.S.*, 1935, 280; *Chem. Abs.*, 1935, 29, 3217; *Brit. Chem. Abs.* A, 1935, 441.

mental measurements of the vapor pressures of these alcohols in dilute aqueous solutions at 25°C.

Isopropyl alcohol forms a large number of constant-boiling binary mixtures with other organic compounds, some of which are listed in Table 89.[17]

Several ternary constant-boiling mixtures containing isopropyl alcohol are known. Thus water, benzene and the alcohol form a composition boiling at 66.5°C. and containing 18.6 per cent moles of alcohol and 56.5 per cent moles of benzene. A combination of 52.7 per cent moles of cyclohexane, 21.8 per cent moles of alcohol and 25.5 per cent moles of water has a boiling point of 66.1°C. Another fluid containing 54.8 per cent moles of cyclohexane, 19.2 per cent moles of isopropyl alcohol and 26.0 per cent moles of water, has a constant boiling point, at normal pressure, of 64.3°C.

The physical characteristics of a number of binary mixtures containing isopropyl alcohol as one component have been recorded. These include mixtures of the alcohol with acetone,[17a] ethyl alcohol,[18] acetaldehyde or heptaldehyde,[19] and benzene.[20] Olsen and Washburn[21] have determined freezing point data for solutions of isopropyl alcohol in benzene and also the equilibrium concentrations of the ternary system, isopropyl alcohol-water-benzene, at 25°C., as well as the viscosities of equilibrium mixtures of these three components. See Table 90.

TABLE 90.—*Solubility and Physical Data of the Ternary System Isopropyl Alcohol-Water-Benzene.*

Weight Percentages of Components in Equilibrium					
Benzene	Alcohol	Water	Refractive Index	Density	Relative Viscosity
99.93	0.00	0.07	1.49750	0.8733	0.674
87.74	13.20	0.06	1.47588	.8594	0.671
82.06	17.22	0.72	1.47295	—	—
68.63	28.54	2.83	1.45493	.8467	0.813
57.81	37.95	4.24	1.44027	.8392	0.935
44.55	46.00	9.46	1.42445	.8405	1.247
35.30	50.28	14.42	1.41317	.8442	1.552
29.40	51.00	19.59	1.40620	.8516	1.893
27.17	51.36	21.47	1.40347	.8543	2.024
23.63	50.42	25.95	1.39865	.8619	2.302
17.59	48.16	34.25	1.39022	.8771	2.830
8.71	41.79	49.50	1.37397	.9084	3.419
6.25	39.11	54.64	1.37041	.9165	3.328
2.21	32.51	65.28	1.36189	.9386	3.061
0.80	25.16	74.04	1.35547	.9571	2.654
0.15	0.00	99.85	1.33289	.9974	1.008

Isopropyl alcohol, when added to gasoline-ethyl alcohol mixtures, brings about a marked increase in the critical water content, i.e., in the water tolerance of such mixtures.

Bayley and Hopkins[22] found that replacement of half the ethanol content of an ethyl alcohol-gasoline blend by isopropanol caused an increase in water tolerance of about 60 per cent at —80°C. and almost 100 per cent at —40°C. This effect is illustrated by the results shown in Table 91. The gasoline in the tests was a commercial motor fuel and did not contain tetraethyl lead. The diluents were dehydrated materials. Benzene is included for comparison.

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[17] B. T. Brooks, *Chem. Industries*, 1933, **33**, 331; *Chem. Abs.*, 1934, **28**, 4871. *World Petroleum Congr., London*, 1933, *Proc.* **2**, 840; *Chem. Abs.*, 1934, **28**, 4871; *Brit. Chem. Abs.* **B**, 1934, 742.

[17a] G. S. Parks and C. S. Chaffee, *J. Phys. Chem.*, 1927, **31**, 439; *Chem. Abs.*, 1927, **21**, 2207; *Brit. Chem. Abs.* **A**, 1927, 405.

[18] G. S. Parks and K. K. Kelley, *J. Phys. Chem.*, 1925, **29**, 727; *Chem. Abs.*, 1925, **19**, 2289; *J.C.S.*, 1925, **128** (2), 764.

[19] H. Adkins and A. E. Broderick, *J.A.C.S.*, 1928, **50**, 499; *Brit. Chem. Abs.* **A**, 1928, 396; *Chem. Abs.*, 1928, **22**, 942.

[20] N. Perrakis, *Compt. rend.*, 1923, **176**, 1137; *Chem. Abs.*, 1923, **17**, 2381. *J. Chim. Phys.*, 1925, **22**, 280; *J.C.S.*, 1925, **128** '2). 764.

[21] A. L. Olsen and E. R. Washburn, *J.A.C.S.*, 1935, **57**, 303; *Chem. Abs.*, 1935, **29**, 2061; *Brit. Chem. Abs.* **A**, 1935, 438.

[22] C. H. Bayley and C. Y. Hopkins, *Can. J. Research*, 1934, **11**, 505; *Brit. Chem. Abs.* **B**, 1935. 86; *J. Inst. Pet. Tech.*, 1934, **20**, 611A; *Chem. Abs.*, 1935, **29**, 401. Also W. R. Ormandy, T. W. M. Pond and W. R. Davies, *J. Inst. Pet. Tech.*, 1934, **20**, 308; *Chem. Abs.*, 1934, **28**, 4862; *Brit. Chem. Abs.* **B**, 1934, 530.

TABLE 91.—*Effect of Third Component on Water Tolerance of Gasoline-Ethanol Mixtures*

Volume Percentages of Components			Critical Water Content Per Cent by Volume		
Gasoline	Ethanol	Third Component	0°C.	-20°C.	-40°C.
90	10	none	0.30	0.22	0.15
90	5	Benzene 5	0.14	0.10	0.07
90	5	Isopropanol 5	>0.45	>0.35	0.28
80	20	none	0.70	0.50	0.35
80	10	Benzene 10	0.36	0.28	0.20
80	10	Isopropanol 10	—	>0.83	>0.65
70	30	none	1.25	0.84	0.59
70	20	Benzene 10	0.94	0.72	0.53
70	20	Isopropanol 10	>1.6	>1.3	1.00

Like other alcohols, isopropanol cannot be mixed with calcium chloride since it forms an addition compound with that reagent. A complex compound with zinc chloride has also been reported.[23] The solubility of a number of inorganic salts, including magnesium bromide and iodide,[24] in isopropyl alcohol has been recorded.

Ferner and Mellon[25] reported data for the solubilities of sodium and potassium chlorides at 16°-35°C. in absolute isopropanol and in aqueous mixtures containing 87.7, 92.6 and 96.5 per cent of this alcohol. The solubilities of calcium, barium and strontium as nitrates at 25°C. in anhydrous isopropyl alcohol were also determined.

Solubilities of the alkali chlorides and sulphates in anhydrous isopropyl alcohol have been measured by Kirn and Dunlap.[26] Anhydrous potassium sulphate was insoluble. Solubilities of the chlorides of both sodium and potassium and the sulphate of the former pass through a maximum solubility with increase in temperature and then decrease. According to Hopkins and Quill,[27] isopropyl alcohol is a very poor solvent for the rare earth chlorides. Neuman[28] determined the solubility of silver bromate in mixtures of isopropyl alcohol and water.

ANALYTICAL REACTIONS OF ISOPROPYL ALCOHOL

The most satisfactory method of detecting and estimating isopropyl alcohol in mixtures consists in oxidation with a sulphuric acid solution of chromic acid followed by distillation and identification of the resulting acetone, which can be also readily estimated volumetrically.[29] Solutions of isopropyl alcohol in water or other non-oxidizable solvents may be quantitatively estimated[30] by chromic acid oxidation. Substitution of the latter by permanganate yields acetone and other products, including carbon dioxide, oxalic acid and acetic acid,[31] so that this reagent is not readily applicable to the quantitative estimation of isopropyl alcohol.

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[23] I. L. Kondakov, F. Balas and L. Vit., *Chem. Listy*, 1929, **23**, 579; 1930, **24**, 126; *Chem. Abs.*, 1930, **24**, 3454; *Brit. Chem. Abs.* A, 1930, 200 and 462.

[24] "International Critical Tables," McGraw-Hill Book Co., New York, 1929, 4, 203.

[25] G. W. Ferner and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 345; *Chem. Abs.*, 1934, **28**, 6385; *Brit. Chem. Abs.* A, 1934, 1193.

[26] E. R. Kirn and H. L. Dunlap, *J.A.C.S.*, 1931, **53**, 391; *Chem. Abs.*, 1931, **25**, 1427; *Brit. Chem. Abs.* A, 1931, 419.

[27] B. S. Hopkins and L. L. Quill, *Proc. Nat. Acad. Sci.*, 1933, **19**, 64; *Chem. Abs.*, 1933, **27**, 3132; *Brit. Chem. Abs.* A, 1933, 456.

[28] E. W. Neuman, *J.A.C.S.*, 1934, **56**, 28; *Brit. Chem. Abs.* A, 1934, 250; *Chem. Abs.*, 1934, **28**, 1247.

[29] S. H. Fleming, Jr., *Mendel Bull.*, 1935, 7, 99; *Chem. Abs.*, 1935, **29**, 5386; *Brit. Chem. Abs.* B, 1936, 404.

[30] H. A. Cassar, *Ind. Eng. Chem.*, 1927, **19**, 1061; *Brit. Chem. Abs.* A, 1927, 1100; *Chem. Abs.*, 1927, 21, 3582.

The xanthate-iodine titration method yields quantitative results in the case of isopropyl alcohol and is also applicable to the determination of other primary and secondary alcohols,[32] provided only one alcohol is present.

According to Brown,[33] a solution of isopropyl alcohol containing 1 per cent vanillin gives a Prussian-blue coloration when treated with 1 to 3 per cent of concentrated sulphuric acid. Different, but distinctive, colorations are exhibited by methyl or ethyl alcohol but amyl alcohol also gives a Prussian-blue color under these conditions. In the absence of other color-producing substances, 1 part in 10,000 of isopropyl alcohol can be detected by this test in mixtures containing it. The manner of conducting the test may be described as follows: Dissolve 0.1 gram vanillin in 10 cc. of the alcohol and allow 1 cc. concentrated sulphuric acid to run down the side of the test tube. With isopropanol, the zone is red below, deep blue above and the mixture is similar to Prussian blue. With amyl alcohol, the zone is dull red below, deep blue above, the mixture is blue and a white precipitate is formed. To differentiate between these two alcohols, add 10 cc. water to each mixture and shake. With isopropanol, the pale blue mixture rapidly turns colorless; with the amyl compound, a grass-green alcoholic upper layer is permanent, even after 2 hours; also a white deposit settles in the colorless aqueous lower layer.

For taxation purposes in India, the term "spirit" includes methyl, ethyl, propyl and isopropyl alcohols. It was found by Aiyar and Krishman[34] that, for the determination of alcohol in mixtures containing isopropanol, the Thorpe and Holmes[35] method failed to give the true alcoholic content. The following modification of the usual procedure was developed by Aiyar and Krishman, to be used with mixtures thought to contain isopropyl alcohol:

To 100 cc. of liquid containing around 30 per cent of "spirit" add common salt to the saturation point. Agitate with 50 cc. petroleum ether (B.P. 40-60°C.) and allow to settle. After drawing off the brine layer, wash the ether extract first with 10 cc. of saturated brine and then with 5 portions of water, combining all these washings with the first salty extract. Collect the first 100 cc. that passes over on distilling the total brine liquor and determine isopropyl alcohol content by specific gravity

Although a sulphuric acid solution of mercuric sulphate (Denigès' reagent) has been suggested as a reagent for the detection of isopropyl alcohol, it has been shown that pure isopropanol gives an entirely negative test and that the yellow precipitate, or coloration, often obtained, is due to impurities in the isopropyl alcohol tested.[36] The most common impurity is tertiary butyl alcohol, which gives an immediate reaction with Denigès' reagent. According to Pukirev,[37] the tertiary butyl alcohol content of isopropyl alcohol is conveniently estimated by comparing the turbidity, or opalescence, obtained by adding 3 cc. of the Denigès' reagent[38] to 0.1 cc. of the isopropyl alcohol solution, with a series of standard solutions. The method is not applicable to concentrations of tertiary butyl alcohol below 0.5 mg. per liter.

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[31] W. M. Evans and L. B. Sefton, *J.A.C.S.*, 1922, **44**, 2271; *Chem. Abs.*, 1923, **17**, 57; *J.C.S.*, 1922, **122**, 1108.

[32] W. F. Whitmore and E. Lieber, *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 127; *Brit. Chem. Abs.* **B**, 1935, 486; *Chem. Abs.*, 1935, **29**, 2878.

[33] C. L. M. Brown, *Pharm. J.*, 1934, **133**, 560; *Brit. Chem. Abs.* **B**, 1935, 137; *Chem. Abs.*, 1935, **29**, 2111.

[34] S. S. Aiyar and P. S. Krishman, *Analyst*, 1935, **60**, 237; *Brit. Chem. Abs.* **B**, 1935, 539; *Chem. Abs.*, 1935, **29**, 3628.

[35] T. E. Thorpe and J. Holmes, *Trans. Chem. Soc.*, 1903, **83**, 314; *J.S.C.I.*, 1903, **22**, 314. This method of analysis is based on the fact that the alcohol in 25 cc. of strong spirit, even when diluted to the extent of 500 cc., can be entirely recovered by distillation, provided the solution is first saturated with common salt. The original alcohol may then be regained in the first 100 cc. of the distillate.

[36] S. H. Fleming, Jr., *Mendel Bull.*, 1935, **7**, 99; *Brit. Chem. Abs.* **B**, 1936, 404; *Chem. Abs.*, 1935, **29**, 3586.

[37] A. G. Pukirev, *J. Applied Chem.* (*U.S.S.R.*), 1935, **8**, 1309; *Brit. Chem. Abs.* **B**, 1936, 181; *Chem. Abs.*, 1936, **30**, 5533.

Buc[39] describes the testing of isopropanol for tertiary butanol by use of Denigès' reagent.[40] The method consists in heating on a water bath for 20 to 30 minutes a mixture of about 10 cc. of an acidified mercuric sulphate solution with about 0.2 cc. of the isopropyl alcohol. If tertiary alcohols are present, a yellow precipitate is formed. The color is distinctive in case of even a few hundredths of one per cent of the impurity. In absence of the trimethyl carbinol, the precipitate is white or only slightly yellowish.

ISOPROPOXIDES

Alkoxides of aluminum have been found to be effective agents[41] for the reduction of aldehydes to the corresponding alcohols. An example of such is the transformation of crotonaldehyde to crotyl alcohol. Acetone is a by-product of these reactions though its removal as fast as formed leads to increased yields of alcohol. Satisfactory production of the alcohol resulted from the employment of benzene (40-45 per cent) and isopropyl alcohol (58-60 per cent) as reacting media. The latter solvent not only gave higher yields but was more convenient, since the propoxide could be prepared in the reaction flask and immediately used without separation and purification.

The aluminum alkoxide gave a 32 per cent yield of citronellol from citronellal and a 68 per cent production of cinnamyl alcohol from cinnamaldehyde.

The investigators made the metallic alkoxide from aluminum amalgam and isopropyl alcohol by a modification of the Adkins method.[42]

Aluminum wire or turnings (100 grams), absolute isopropyl alcohol (1200 cc.) and mercuric chloride (5 grams) are placed in a 2-liter round bottomed flask provided with a reflux condenser. By means of a steam bath, the mixture is gently warmed for 10 or 20 minutes until a gray precipitate is formed. The reaction then becomes so vigorous that external cooling is necessary until this activity ceases. Heating and refluxing is then continued for 6 or 7 hours. The aluminum isopropoxide may then be used for the aldehyde-alcohol reaction described above, or purified by distillation. The yield with the above amounts specified is 645-680 grams (85-90 per cent) of alkoxide, with a boiling point of 145-150°C. (5 mm.).

The aluminum isopropoxide was found in every instance superior to the ethoxides of the same metal or of chloromagnesium for carrying out aldehyde reductions similar to those described above.

INDUSTRIAL APPLICATIONS OF ISOPROPYL ALCOHOL

In addition to its utilization on a comparatively large scale for the production of various chemical products (see below), the main industrial applications of this alcohol are based on its solvent properties for a wide variety of materials. It finds extensive use in the preparation of perfumes, odorants, plant extracts and medicinal products for external use. Although unsuitable, pharmacologically, for internal medication and as a component of mouth washes, this alcohol can be employed advantageously in the preparation of various cosmetics. Vapon, used as a hair wash or shampoo fluid, contains a high percentage of isopropyl alcohol.[43]

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[38] G. Denigès, *Compt. rend.*, 1898, 126, 1145, 1277; *J.C.S.*, 1898, 74 (1), 618; *J.S.C.I.*, 1898, 17, 697.

[39] H. E. Buc, U. S. P. 1,911,798, May 30, 1933, to Standard Oil Development Company; *Brit. Chem. Abs.* B, 1934, 186; *Chem. Abs.*, 1933, 27, 3943.

[40] An aqueous solution containing 20 grams of mercuric sulphate and 50 cc. of concentrated sulphuric acid per liter.

[41] W. G. Young, W. H. Hartung and F. S. Crossley, *J.A.C.S.*, 1936, 58, 100; *Brit. Chem. Abs* A, 1936, 316; *Chem. Abs.*, 1936, 30, 1737.

[42] H. Adkins, *J.A.C.S.*, 1922, 44, 2178; *Chem. Abs.*, 1922, 16, 4116; *J.S.C.I.*, 1923, 42, 71A.

Pharmacology. Isopropanol has been accepted for admission to the approved list of New and Non-official Remedies by the U. S. Council of Pharmacy and Chemistry.[44] The alcohol may be used for the removal of creosote from the skin as a prophylactic agent against creosote burns.[45] It is also recommended for disinfection of the skin and of hypodermic syringes and needles. It may be employed as a disinfecting agent in the administration of insulin. However, the alcohol cannot be relied upon to destroy such spore-forming organisms as *Clostridium tetan*, *Clostridium welchii* or *Bacillus anthracis*. Isopropanol for uses noted above must conform with three tests, *viz.*,

Total solids. Not more than 0.01 per cent residue is allowable after drying, at 100°C., the material obtained by evaporation of 100 cc. of the alcohol in a platinum dish on a water bath.

Aldehyde. Treat 20 cc. of the alcohol with 1 cc. of freshly prepared ammonio-silver nitrate solution by shaking thoroughly in a stoppered test-tube and allowing to stand for at least six hours in diffused daylight. No more than a faint cloudiness or tinge of brownish color is tolerated.

Acetone should be absent. If present, a purplish red color is obtained by the following procedure. Mix thoroughly 5 cc. alcohol, 2 cc. of 1*N* sodium hydroxide solution and 5 drops of a 1 per cent sodium nitroprusside solution; then acidify carefully with acetic acid.

According to Westermann,[46] isopropyl alcohol has a higher disinfecting value than ethyl alcohol, a 50 per cent solution of the former having about the same power as a 70 per cent solution of the latter. For sterilization of the hands, a 30 per cent solution of isopropyl alcohol, containing 1 per cent of the soap preparation known as Baktol, is very efficient, having no unpleasant odor and no injurious action on the skin.

For the stabilization of egg material to be used in shampoo mixtures, isopropyl alcohol and other monohydric alcohols are added in a proportion of 7.5 to 20 per cent of the water present in the finished product.[47]

Isopropanol has been proposed as a precipitating agent for the elimination of asphalt from petroleum oils.[48] For this purpose the alcohol should be practically anhydrous. Similarly, the dewaxing of lubricating oils may be accomplished by treatment with *sec*-butyl acetate that contains 10-25 per cent by volume of isopropyl alcohol.[49] The mixture should be chilled to precipitate the wax.

Isopropyl alcohol and secondary butyl alcohol have been suggested as effective in the separation of sulphonates from the acid sludge obtained by sulphuric acid treatment of hydrocarbons. The sludge is washed with water, neutralized and then extracted with the solvent. Separation takes place into three portions: namely, a tarry material, a solution of inorganic salts and a third layer containing a solution of sulphonates in the solvent.[50]

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[43] T. Ruemele, *Seifensieder-Ztg.*, 1936, **63**, 21; *Chem. Abs.*, 1936, **30**, 1517.

[44] Council of Pharmacy and Chemistry, *J. Am. Med. Assoc.*, 1935, **105**, 1684; *Chem. Abs.*, 1936, **30**, 1947.

[45] A dosage form (2 cc. and 15 cc. ampules) intended solely for the removal of creosote from the skin, is now available under the designation. "Saf-T-Top Isopropyl Alcohol, 98%."

[46] W. Westermann. *Hyg. Infekt. Krank.*, 1933, **115**, 154; *Chem. Zentr.*, 1933, **2**, 909; *Brit. Chem. Abs.* **B**, 1933, 654; *Chem. Abs.*, 1933. **27**, 4554.

[47] C. J. Beckert, W. Kritchevsky and B. R. Harris, U. S. P. 1,924,972, Aug. 29, 1933; *Chem. Abs.*, 1933, **27**, 5484; *Brit. Chem. Abs.* **B**, 1934, 556.

[48] French P. 785,349, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 608.

[49] A. M. Wilson, U. S. P. 2,049,036, July 28, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 6550; *J. Inst. Pet. Tech.*, 1936, **22**, 457A.

[50] French P. 748,422, 1933, to Standard Oil Development Co.; *Chem. Abs.*, 1933, **27**, 5530.

Isopropanol as a Non-Solvent in Rubber Cements. A systematic study of the effects of a number of non-solvents on rubber cements has been made by Ford.[51] The use of ethyl alcohol for reducing the apparent viscosity of such compositions is an established practice, though acetone and amyl acetate are known to function in the same manner. The experiments reported were concerned with the control of film-thickness on dipped articles and the tendency of wet films to break across small holes in perforated objects. The commercial benzene cement utilized for the trials originally contained 250 grams of non-volatile ingredients per liter of finished product. The addition of non-solvents to the cement improved the film-breaking tendency. The various liquids tested for this purpose could be arranged in the following order of decreasing effectiveness: isopropanol, ethanol, Pentasol (technical), butanol (technical), amyl and butyl acetates, acetone, methyl ethyl ketone and benzene. Volume for volume there was no difference in this respect between the first two alcohols named, but more than 10 per cent of ethanol caused coagulation, while over 15 per cent of isopropanol could be present without such coalescence occurring. In deposited films wide variations in alcohol content due to evaporation of benzene-ethanol mixtures tend to irregular breaking of films but this trouble is eliminated by the use of isopropanol. The maximum film-breaking effect resulted on use of cements containing about 11 per cent (by volume) of isopropyl alcohol. This addition resulted, however, in reduction of film thickness, which could be offset by a longer mastication period for the rubber stock and a variation of non-volatile ingredients. It was found that below about 33 per cent (by volume), isopropanol is not completely dissolved in benzene. This same ratio was shown to exist beween isopropanol and total solvent just where coagulation of the cement occurred. About 50 parts of isopropyl alcohol to 100 parts benzene were necessary for the formation of a clear solution. In the wet cement film Ford considered the isopropanol to exist in a state of very fine dispersion.

Anti-Freeze Mixtures. An important commercial application of isopropyl alcohol is in the preparation of anti-freeze compositions for automobile radiators. For this purpose a 65:35 blend of isopropyl and methyl alcohols is being marketed.[52] The mixture is reported to be superior to ethyl alcohol for this purpose since, on dilution with water, it does not attack metal parts, rubber or varnishes.[53] A similar anti-freeze composition disclosed by Howard[54] consists of 75 to 55 per cent by volume of isopropanol with 25 to 45 per cent methyl alcohol. When diluted with water, this mixture is said to duplicate substantially the density, volatility and freezing point of an aqueous solution containing an equivalent proportion of ethyl alcohol.

The addition of a small quantity of a petroleum distillate of density greater than 0.8 and boiling point higher than 300°C., to anti-freeze compositions of this type is proposed for detecting their dilution. The mixture becomes milky on addition of less than 5 per cent of water.[55]

Berliner[56] states that anti-freeze compositions containing aliphatic alcohols may be rendered non-corrosive by the addition of a small proportion (0.1-0.5 per cent) of an alkyl (or aryl-) antimonyl tartrate. Amino-derivatives of these compounds are also effective for this purpose.

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[51] T. F. Ford, *Ind. Eng. Chem.*, 1936. **28**, 915; *Chem. Abs.*, 1936, **30**, 7385.

[52] Stanco Inc., see *Chem. Trade J.*, 1933, **93**, 162.

[53] See, for example, *Oesterreich. Chem. Ztg.*, 1935, **38**, 38; M. Nemirovich, *Novosti Tekhniki Seriya Gorno-Rudnaya Prom.*, 1935, No. 13, 4; *Chem. Abs.*, 1935, **29**, 6326; *Brit. Chem. Abs.* **B**, 1936, 719.

[54] F. A. Howard, U. S. P. 1,955,296, April 17, 1934, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1935, 2; *Chem. Abs.*, 1934, **28**, 3852.

[55] P. K. Frolich and S. P. Gildersleeve, U. S. P. 1,919,628, July 25, 1933, to Standard Oil Development Co., *Brit. Chem. Abs.* **B**, 1934, 304; *Chem. Abs.*, 1933, **27**, 4893.

[56] J. F. T. Berliner, U. S. P. 1,956,266, April 24, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 2; *Chem. Abs.*, 1934, **28**, 4194.

Some investigations seem to indicate that isopropyl alcohol may find application in gasoline mixtures for use as motor fuels. Thus, as previously mentioned, Bayley and Hopkins[57] show that addition of isopropyl alcohol to gasoline-ethyl alcohol mixtures results in a marked increase in the critical water content of such compositions. Ormandy, Pond and Davies[58] studied the blending behavior of isopropyl, *n*-butyl, isobutyl and tertiary butyl alcohols with a typical gasoline and with certain motor fuel hydrocarbons. They concluded that isopropyl alcohol had the best all-round mixing properties of any of the above named substances.

Another possible application of isopropyl alcohol is as an agent for removing ice from airplane carburetors.[59]

Isopropanol as a Solvent. On account of its cheapness and freedom from tax restrictions, isopropyl alcohol is now being used extensively in chemical analysis in place of ethanol which is not only more costly but often inconvenient on account of the precautions necessary to prevent its illicit diversion. The applications in analytical chemistry have been reviewed by Ferner and Mellon,[60] who found that it was an effective solvent in a number of analytical tests, for example, in preparing solutions of dimethylglyoxime, 8-hydroxyquinoline and alpha-benzoinoxime. Schuette and Harris[61] used isopropyl alcohol as a solvent for potassium hydroxide. Ferner and Mellon found that $0.1N$ solutions were stable but $0.5N$ solutions developed a color even in the dark.[62] Isopropanol may replace ethanol in the qualitative test for chromates involving reduction to green tervalent chromium. However, it proved unsatisfactory as a substitute in the flame test for borates and in the acetate test given by the U. S. Pharmacopeia. Several examples of the use of isopropyl alcohol in the separation of inorganic salts have been given by Ferner and Mellon. Included were the separation of calcium nitrate from barium nitrate, of calcium oxide from magnesium oxide and of alkali chlorides from magnesium chloride.

CHEMICAL DERIVATIVES OF ISOPROPYL ALCOHOL

Acetone. The production of acetone from isopropyl alcohol by catalytic dehydrogenation is now carried out commercially on a large scale.[63] In addition to acetone, a number of other derivatives of isopropyl alcohol, including various esters, diisopropyl ether and isopropyl phenols, are finding important applications in industry.

Esters of Isopropyl Alcohol. Table 92 summarizes the physical constants of a number of isopropyl esters of organic and inorganic acids.

Organic Esters. Isopropyl esters of organic acids are usually prepared by direct interaction of the alcohol carboxylic acid in the presence of a condensing agent, such as sulphuric acid. They may, however, be obtained directly from

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[57] C. H. Bayley and C. Y. Hopkins, *Can. J. Research*, 1934, 11, 505; *Brit. Chem. Abs.* **B**, 1935, 86; *J. Inst. Pet. Tech.*, 1934, **20**, 611A; *Chem. Abs.*, 1935, **29**, 401.

[58] W. R. Ormandy, T. W. M. Pond and W. R. Davies, *J. Inst. Pet. Tech.*, 1934, **20**, 308; *Chem. Abs.*, 1934, **28**, 4862; *Brit. Chem. Abs.* **B**, 1934, 530.

[59] *Cf.* A. Swan, *Aircraft Engineering*, 1936, **8** (83), 3; *J. Inst. Pet. Tech.*, 1936, **22**, 110A.

[60] G. W. Ferner and M. G. Mellon, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 345; *Chem. Abs.*, 1934, **28**, 6385; *Brit. Chem. Abs.* **A**, 1934, 1193.

[61] H. A. Schuette and L. E. Harris, *J. Amer. Pharm. Assoc.*, 1926, **15**, 166; *Brit. Chem. Abs.* **B**, 1927, 118; *Chem. Abs.*, 1926, **20**, 3827.

[62] H. A. Schuette and M. P. Smith, (*Ind. Eng. Chem.*, 1926, **18**, 1242; *Chem. Abs.*, 1927, **21**, 661; *Brit. Chem. Abs.* **B**, 1927, 117) used isopropyl alcohol in the determination of acid and saponification numbers in place of ethyl alcohol solvent.

[63] A discussion of these methods is given in Chapter 18.

TABLE 92.—*Properties of Inorganic and Organic Esters of Isopropyl Alcohol.*[64]

Compound	Boiling Point, °C. at 760 mm.	$d^{t°C.}_{4°C.}$
Isopropyl chloride	36.5	0.860 (20°C.)
Isopropyl bromide	59.6	1.310 (20°C.)
Isopropyl iodide	89.5	1.703 (20°C.)
Isopropyl mercaptan	60	—
Isopropyl thioether	120.4	—
Diisopropyl sulphate[a]	80 (at 3.7 mm.)	1.1155 (15°C.)
Isopropyl formate	71.3	0.883 (0°C.)
Isopropyl acetate	89.0	0.869 (25°C.)
Isopropyl propionate	111.3	0.893 (0°C.)
Isopropyl *n*-butyrate	128	0.865 (13°C.)
Isopropyl isobutyrate	120.8	0.869 (0°C.)
Isopropyl lactate	80 (at 32 mm.)	—
Isopropyl chloroacetate[b]	149.5	1.092 (20°C.)
Isopropyl benzoate	218.5	1.017 (15°C.)

[a] W. R. Ormandy and E. C. Craven, *J. S. C. I.*, 1930, **49**, 362T; *Chem. Abs.*, 1930, **24**, 5714; *Brit. Chem. Abs.* **A**, 1930, 1404.

[b] R. C. Roark and R. T. Cotton, *Ind. Eng. Chem.*, 1928, **20**, 512; *Chem. Abs.*, 1928, **22**, 2434; *Brit. Chem. Abs.* **B**, 1928, 497.

propene by treatment with organic acids in the presence of catalysts or from isopropyl sulphate liquors by reaction with the corresponding acids.[65]

Nazarov and Khain[66] consider petroleum sulphonic acid to be a more effective condensing agent for isopropanol and acetic acid than sulphuric acid. The highest yield of isopropyl acetate was 94 per cent of the original acetic acid treated. The reactants were mixed in the ratio of 4.22 parts of alcohol to one of acid. The temperature was 105-110°C. and the feed rate 1 cc. per min. With technical products the proportions of alcohol and acid would be 5.2:1 in which case the yields would be 42 per cent based on the anhydrous acid or 58 per cent, on the commercial acetic acid. No gases or polymers were formed and there was no dehydration of the alcohol which was reported to be 98 per cent converted. Of the petroleum sulphonic acids, approximately 8.2 grams sufficed for the production of one kg. of isopropyl acetate. Even then the catalyst was only slightly weakened. Dried catalysts and the technical form were equally effective. Nazarov and Khain call attention to the cheapness of the petroleum sulphonic acids in comparison with sulphuric acid, generally used.

Boron trifluoride is likewise a catalyst both for the esterification of isopropyl alcohol and for the direct condensation of propene and organic acids.[67] For example, yields of 16.8, 38.8, 48.6, 57.8 and 60 per cent, respectively, of the corresponding isopropyl esters were obtained from acetic, mono, di-, trichloroacetic and benzoic acids by treatment with isopropanol and boron trifluoride. Equimolar proportions of each acetic acid and the alcohol were refluxed for three hours with 3 g. of boron trifluoride per mole of acid. Equal weights of benzoic acid and the alcohol were under reflux for 50 minutes. When a solvent or suspension medium (such as carbon tetrachloride) was incorporated with the chloroacetic acid and the mixture agitated, complete esterification took place in one hour.

It is of interest that these workers obtained the same esters in yields of 7.0, 34.2, 39.5, 48.8 and 88.0 per cent, respectively, by combination in turn of the acids mentioned above, with propene in presence of boron trifluoride. Addition took place at 70°C. under a pressure of about 25 cm. of mercury above atmospheric.

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[64] Data from International Critical Tables, McGraw-Hill Book Co., Inc., New York, 1926.

[65] The direct esterification of olefins is discussed in Chapter 12.

[66] S. A. Nazarov and S. S. Khain, *Mat. on Cracking*, 1935, No. 2, 183; *Brit. Chem. Abs.* **B**, 1936, 631; *Chem. Abs.*, 1935, **29**, 6032.

[67] T. B. Dorris, F. J. Sowa and J. A. Nieuwland, *J.A.C.S.*, 1934, **56**, 2689; *Brit. Chem. Abs.* **A**, 1935, 195; *Chem. Abs.*, 1935, **29**, 724.

Attention was called, by these investigators, to the fact that Sudborough and Lloyd[68] reported results which were in the reverse order on using hydrochloric acid to catalyze the same esterifications with isopropyl alcohol as those reported above.

Isopropyl acetate has been obtained by Sowa and Nieuwland[69] on interaction of isopropyl with the addition compound of acetamide and boron trifluoride. The yield seemed to depend on the amount of the fluoride used, so long as an excess of the addition compound was avoided. The methathesis which took place is indicated by the equation

$$CH_3CONH_2 \cdot BF_3 + (CH_3)_2CHOH \longrightarrow CH_3COOCH(CH_3)_2 + BF_3 \cdot NH_3$$

Formation of the amino boron fluoride was considered to be the "driving force" of the reaction. The acetamide-boron fluoride addition was accomplished by passing one mole of the metallic fluoride into a 500 cc. flask containing one mole of acetamide. On introduction of one mole of isopropyl alcohol the amino boron fluoride soon separated as a white solid. After refluxing the mixture for about half an hour, the isopropyl acetate could be distilled directly from the reaction vessel through a fractionating column. A 32 per cent yield was obtained. Analysis of the solid residue showed it to contain one mole of ammonia. Practically all the boron fluoride could be recovered by heating the residue, after removal of organic matter, with concentrated sulphuric acid.

This and similar esters may also be produced by reacting diisopropyl ether with the required aliphatic monocarboxylic acid in the presence of catalytic proportions of a strong non-volatile acid, such as sulphuric. The process is most successful when carried out by heating under pressure.[70] For instance, diisopropyl ether and acetic acid, when heated to about 120°C., furnish isopropyl acetate if 2 to 4 per cent sulphuric acid is included as a condensing agent.

Merley[71] proposes rectification in the absence of water to remove impurities. such as hydrocarbons and mercaptans, from esters. The latter is then redistilled (to eliminate entrained material) with a constant proportion of water at substantially atmospheric pressure. The purification is completed by drying the ester.

Secondary alkyl esters of polycarboxylic acids of relatively high boiling point, such as isopropyl phthalate, have been recommended[72] as heat-transmitting agents. Isopropyl esters of the acids obtained by oxidizing paraffin wax, are suggested as components of a rinsing oil for motors.[73]

Isopropyl bromide may be produced in the laboratory by heating isopropyl alcohol with potassium bromide and sulphuric acid. It has been shown by Werner[74] that considerable amounts of propene are formed when using concentrated acid for this reaction, in which case poor yields (38 per cent) of ester are obtained. The formation of olefin can be suppressed by dilution with at least 10 per cent of water. On heating 100 g. of a 3:1 molar mixture of isopropanol and water, 150 g. concentrated sulphuric acid and 210 g. of sodium bromide dihydrate to 90°-115°C., a 73.5 per cent yield of isopropyl bromide resulted, without olefin production.

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[68] J. J. Sudborough and L. L. Lloyd, *J.C.S.*, 1899, **75**, 467; *Chem. Ztg.*, 1899, **1**, 522; *Chem. Zentr.*, 1899, **1**, 1154.

[69] F. J. Sowa and J. A. Nieuwland, *J.A.C.S.*, 1933, **55**, 5052; *Brit. Chem. Abs.* **A**, 1934, 176; *Chem. Abs.*, 1934, **28**, 740.

[70] H. L. Cox and P. S. Greer, U. S. P. 2,030,835, Feb. 11, 1936, to Union Carbide and Carbon Corp.; *Chem. Abs.*, 1936, **30**, 2200; French P. 794,715, 1936; *Chem. Abs.*, 1936, **30**, 5236.

[71] S. R. Merley, U. S. P. 1,928,132, Sept. 26, 1933, to Doherty Research Co.; *Chem. Abs.*, 1933, **27**, 5753; *Brit. Chem. Abs.* **B**, 1934, 750.

[72] L. Rosenstein, U. S. P. 2,006,411, July 2, 1935, to Shell Development Co., *Chem. Abs.*, 1935, **29**, 5313; *Brit. Chem. Abs.* **B**, 1936, 911.

[73] French P. 781,982, May 25, 1935, to Standard Oil Development Co., *Chem. Abs.*, 1935, **29**, 7065.

[74] E. A. Werner, *J.S.C.I.*, 1933, **52**, 285T; *Brit. Chem. Abs.* **A**, 1933, 1139; *Chem. Abs.*, 1934, **28**, 4374.

The rate of hydrolysis of isopropyl bromide in alkaline media is unimolecular in very low hydroxyl ion concentrations (e.g., 0.005*N* sodium hydroxide) but at higher concentrations (for example, 0.1*N* sodium hydroxide), a bimolecular substitution reaction takes place accompanied by elimination of propene as a second-order reaction.[75]

Sodium isopropyl xanthate is reported as having a number of uses commercially, e.g., as accelerator in rubber vulcanization, in the preparation of insecticides and in flotation processes.[76]

ISOPROPYL ETHER

Isopropyl ether is rapidly assuming a role of importance in chemical industry. Next to acetone, it may prove the most valuable commercially of the derivatives of isopropanol. It is obtained as a by-product in the manufacture of isopropyl alcohol by the acid absorption process, whenever substantial proportions of diisopropyl sulphate are present in the reaction liquor.

A distillation process for the separation of mixtures of isopropyl ether and isopropanol has been described.[77] Enough water is maintained in the liquor to give a constant boiling minimum mixture, in this case 9 parts of isopropyl ether to 1 part of water, (b.p. 73-74°C.). Addition or return of water is stopped in time to avoid carrying over isopropyl alcohol which remains in the still.

Another procedure for preparing the ether involves treatment of propene, under pressures of 3.5 to 35 kg. per sq. cm., with 70-85 per cent sulphuric acid at temperatures up to 50°C.[78] The product may then be recovered by reducing the pressure to 1 atmosphere (*ca.* 1 kg. per sq. cm.) and increasing the temperature to 100-125°C. However, isopropyl ether is often made by dehydration of the corresponding alcohol under the influence of sulphuric acid. Brik[79] has described a continuous process utilizing this reaction by heating 100 parts of isopropyl alcohol with 37.5 parts of 100 per cent sulphuric acid. A yield of 43.5 per cent was secured and the ether could be separated from the distillation product by three successive washings with 2 volumes of water.

Physical Data for Isopropyl Ether. The physical characteristics of this compound are summarized[80] in Table 93.

TABLE 93.—*Physical Constants of Isopropyl Ether.*

Boiling point at 760 mm.	153-158°F. (67-70°C.)
d_4^{20}, at 20°C. (68°F.)	0.725
Refractive index at 20°C. (68°F.)	1.3680
Freezing point	−125°F. (−87°C.)
Viscosity, centipoise at 68°F.	0.322
Latent Heat of Vaporization, B.t.u. per lb.	123
Low value of Heat of Combustion, B.t.u. per lb.	15,600
Reid Vapor Pressure, lbs. per sq. in. at 100°F.	5.3

Effect of Sulphuric Acid on Ethers. The solubilities of a number of ethers at 20°C. in various concentrations of sulphuric acid have been determined by Kirrmann and Graves.[81] The amounts of the ethers found in 100 volumes of solution are given for ethyl, *n*-propyl, isopropyl and two mixed isopropyl ethers in Table 94.

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[75] E. D. Hughes, C. K. Ingold and U. G. Shapiro. *J.C.S.*, 1936, 225; *Brit. Chem. Abs.* **A**, 1936, 433; *Chem. Abs.*, 1936, **30**, 2913.

[76] L. Rosenstein, U. S. P. 2,037,437, April 14, 1936; *Chem. Abs.*, 1936, **30**, 3835.

[77] French P. 792,878, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 4180. British P. 444,117, 1936; *Chem. Abs.*, 1936, **30**, 5237; *Brit. Chem. Abs.* **B**, 1936, 733.

[78] French P. 793,482, 1936, to Standard Alcohol Co.; *Chem. Abs.*, 1936, **30**, 4516. See also Chapter 14.

[79] A. N. Brik, *Trudui Tzentral Nauch.-Issledovatel. Lesokhim. Inst. Narkomlesa U.S.S.R.* (*Trans. Central Inst. Sci. Research Forest Chem. U.S.S.R.*), 1933, **1**, 148; *Chem. Abs.*, 1934, **28**, 3712; *Brit. Chem. Abs.* **A**, 1934, 1199.

[80] H. E. Buc and E. E. Aldrin, *Refiner*, 1936, **15**, 301. *Nat. Pet. News*, 1936, **28** (25), 25; *Chem. Abs.*, 1936, **30**, 6177; *S. A. E. Journal*, 1936, **39**, 333, 357T; *Chem. Abs.*, 1936, **30**, 7828. *Automotive Industries*, 1936, **74** (26), 913; *Oil and Gas J.*, 1936, **35** (5), 41; *J. Inst. Pet. Tech.*, 1936, **22**, 354A.

TABLE 94.—*Solubilities of Ethers in Dilute Sulphuric Acid.*

Ether	Volumes of Ether per 100 Volumes of Solution in Sulphuric Acid of Concentration				
	39%	47%	55%	65%	82%
Diethyl	11	37	53	74	85
Dipropyl	—	—	2	60	81
Diisopropyl	—	—	—	63	—
Propyl isopropyl	—	—	—	65	81
Butyl isopropyl	—	—	—	62	83

Both ethyl and *n*-propyl ether were unaffected by equal volumes of concentrated sulphuric acid. The other ethers tested were subject to slow decomposition by such treatment, the isopropyl being attacked at the same rate as the mixed ethers. After 5 cc. of 92 per cent sulphuric acid had reacted with 4 cc. of isopropyl ether for 3 days, only 1.1 cc. of the latter could be recovered.

Because of the action of sulphuric acid noted above, some details of methods for preparing other alkyl ethers are of especial interest. For example, studies[82] of the equilibrium between dimethyl ether, methanol and water, using a potassium-alum catalyst, indicated an 88.7 per cent conversion of anhydrous alcohol to ether at 230°C. A 99.3 per cent yield was possible with sulphuric acid as activator at 130°C., but above this point dimethyl sulphate was formed. Dehydration of normal propyl alcohol in vapor phase by means of potassium-alum showed a maximum, 84 per cent, conversion to normal propyl ether at 190°C. It has been noted that propyl ether is more stable at 230° than the corresponding alcohol.[83] This is considered an indication that the normal ether cannot be the intermediate product when propene is made by dehydration of propyl alcohol.

USES OF ISOPROPYL ETHER

Solvent. Isopropyl ether may be employed industrially in solvent extraction operations. Thus, Reid[84] has disclosed the use of this ether, alone or in admixture with other solvents, for the precipitation of wax from petroleum oils. For example, 30 gallons of wax distillate were dissolved in a mixture of 60 gallons of isopropyl ether and 40 gallons of acetone After cooling the solution to 0°C., the precipitated wax was filtered off, washed with a small amount of solvent and dried. The lubricating oil recovered after distillation of the solvent had a pour point near 0°C.

Govers[85] has found a combination of 3 parts isopropyl ether and 2 parts aniline to have a selective action, at low temperatures, on the liquid hydrocarbons of wax-bearing mineral oils. The viscous raw material is incorporated with the solvent and cooled to about −18°C. After removing the precipitated waxes, most of the ether is vaporized from the dewaxed liquid. A second extraction is then carried out with aniline alone. The resultant mixture, at about 15°C., can be divided into extract and raffinate phases. By removal of solvent from the latter, a low-pour-test lubricating oil of high viscosity is obtained.

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[81] A. Kirrmann and M. Graves, *Bull. soc. chim.*, 1934, (5) 1, 1494; *Chem. Abs.*, 1935, **29**, 2516; *Brit. Chem. Abs.* **A**, 1935, 203.

[82] N. G. Gajendragad, S. K. K. Jatkar and H. E. Watson, *J. Indian Inst. Sci.*, 1932, **15A**, 59; *Chem. Abs.*, 1933, **27**, 654; *Brit. Chem. Abs.* **A**, 1933, 25.

[83] N. G. Gajendragad and S. K. K. Jatkar, *J. Indian Chem. Soc.*, 1935, **12**, 486; *Chem. Abs.*, 1936, **30**, 362; *Brit. Chem. Abs.* **A**, 1935, 1349.

[84] E. W. Reid, U. S. P. 1,947,359, Feb. 13, 1934, to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1934, 1047; *J. Inst. Pet. Tech.*, 1934, **20**, 334A; *Chem. Abs.*, 1934, **28**, 2515.

[85] F. X. Govers, U. S. P. 2,044,721, June 16, 1936, to Indian Refining Co.; *Chem. Abs.*, 1936, **30**, 5782; *J. Inst. Pet. Tech.*, 1936, **22**, 407A.

Carruthers[86] recommends isopropyl ether for the extraction of dialkyl sulphates from acid liquors resulting from absorption of olefins in recovered acid containing carbonaceous polymerization products.

Before cooling hydrocarbon oils to cause deposition of wax, Sullivan[87] proposes to add a diluent consisting of methyl acetate, 30 parts, and isopropyl ether, 70 parts.

Other uses for this ether are as a solvent,[88] either alone or admixed with ethyl acetate,[89] in the extraction (from dilute aqueous solutions) of aliphatic acids (e.g., acetic), as a precipitating medium (for molding powders made from cellulose acetate) when admixed with acetic acid,[89a] and as an ingredient (to the extent of 1 to 5 per cent) of a cleaning solution of which the other components consist of 85 per cent of a mixture of phosphoric acid, ethyl alcohol and water.[90] The latter composition is said to be effective in the prevention of rust on materials made of iron.

Isopropyl Ether a High-octane Blending Agent. The discovery has been made that isopropyl ether, unlike ethyl ether, possesses high anti-detonating properties when mixed with gasoline. This ether thus becomes of value as a supplementary material to isooctane in the production of high-octane motor fuels, particularly aviation gasolines. According to Buc and Aldrin,[91] a mixture of 60 per cent aviation gasoline (octane number about 74) and 40 per cent isopropyl ether has an octane number of 100 when only 3 cc. of tetraethyl lead per gallon are added. This blend has a minimum specific fuel consumption 5 to 7 per cent higher under cruising conditions than the usual 100-octane isooctane blend while the power outputs and consumptions under high-power conditions are similar. The blending value of isopropyl ether is said to be slightly better than that of technical isooctane irrespective of the presence or absence of lead tetraethyl in the fuel under investigation.

UNSTABLE PEROXIDES FROM ETHERS

The tendency of ethers to form unstable peroxides has been emphasized by a number of investigations. In 1933, Robertson[92] stated that an explosion had taken place during distillation of some isopropyl ether. He noted the similarity of the circumstances and effects to those reported frequently with ethyl ether and attributed to the presence of peroxides.

In 1936, Morgan and Pickard[93] reported two violent explosions caused by accumulated peroxides in isopropyl ether. In one case, 100 cc. of ether that had been stored at least 4 years was being distilled on an electrically heated water bath. When the liquid did not seem to be boiling smoothly, the flask was gently shaken (assuming the liquid might be superheated) whereupon the explosion took place. Another sample of this ether gave peroxide reactions with acidified solutions of potassium iodide or permanganate and was found to contain large quantities of decomposition products.

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[86] T. F. Carruthers, U. S. P. 1,949,366, Feb. 27, 1934; *Chem. Abs.*, 1934, **28**, 2731; *Brit. Chem. Abs.* B, 1935, 13.

[87] F. W. Sullivan, Jr., U. S. P. 1,938,545, Dec. 5, 1933, to Standard Oil Co. of Ind.; *Brit. Chem. Abs.* B, 1934, 869; *Chem. Abs.*, 1934, **28**, 1180.

[88] J. A. Jenemann, U .S. P. 1,906,068, April 25, 1933, to Grasselli Chemical Co.; *Brit. Chem. Abs.* B, 1934, 86; *Chem. Abs.*, 1933, 27, 3485.

[89] G. P. Lunt, U. S. P. 1,958 898, May 15, 1934, to E. B. Badger & Sons Co.; *Brit. Chem. Abs.* B, 1935, 262; *Chem. Abs.*, 1934, **28**, 4434.

[89a] C. J. Malm and C. R. Fordyce, U. S. P. 2,000,601, May 7, 1935, to Eastman Kodak Co., *Chem. Abs.*, 1935, **29**, 4174.

[90] W. K. Schweitzer, U. S. P. 1,949,921, Mar. 6, 1934, to Grasselli Chemical Co.; *Chem. Abs.*, 1934, **28**, 3049; *Brit. Chem. Abs.* B, 1935, 315.

[91] H. E. Buc and E. E. Aldrin, *Refiner*, 1936, 15, 301. *Nat. Pet. News*, 1936, **28** (25), 25; *Chem. Abs.*, 1936, **30**, 6177; *S.A.E. Journal*, 1936, **39**, 333, 357T; *Chem. Abs.*, 1936, **30**, 7828; *Automotive Industries*, 1936, **74** (26), 913; *Oil and Gas J.*, 1936, **35** (5), 41; *J. Inst. Pet. Tech.*, 1936, **22**, 354A. Such a gasoline is said to meet the requirements of the U. S. Army, U. S. Navy and British Air Ministry.

[92] R. Robertson, *Chem. & Ind.*, **1933**, 274; *Brit. Chem. Abs.* B, 1933, 487.

[93] G. T. Morgan and R. H. Pickard (with D. V. N. Hardy); *Chem. & Ind.*, **1936**, 421; *Brit. Chem. Abs.* B, 1936, 732; *Chem. Abs.*, 1936, **30**, 5416.

Later, some diisopropyl ether had been used to remove small amounts of organic acids from an aqueous solution, and 50 cc. of the extract after drying, was being distilled over an electric heater. When about all the ether had distilled, a white fume appeared and the heat was switched off. An explosion followed shortly. This specimen of ether had been in stock 5 years and contained 8 per cent of higher boiling substances which gave the following tests for peroxides: (1) permanganate solution reduced to hydrated manganese dioxide, with liberation of oxygen; (2) mercury rapidly oxidized to a brownish black powder; (3) iodine liberated from aqueous potassium iodide. Morgan and Pickard advise testing all ether specimens of old or doubtful age for liberation of iodine from aqueous potassium iodide. In case peroxides are present, they may be safely removed by exhaustive treatment with either mercury or aqueous permanganate.

Williams[94] reports that practically all ethers formed peroxides on storage and that explosions have resulted in many instances when distillation of such liquids was attempted. He considers diethyl, diisopropyl, ethyl-*ter*-butyl, and ethyl-*ter*-amyl ethers may prove hazardous. Others, such as methyl-*ter*-butyl, methyl-*ter*-amyl or methyl-*ter*-hexyl, which may be distilled without appreciable danger, even after considerable storage periods are classed as less hazardous.[95] He recommends steam distillation, particularly in the presence of a small quantity of alkali, even though antitoxidants (e.g., α- or β-naphthol or hydroquinone) have been incorporated with the ether prior to storage.

The following procedure is given for the quantitative determination of peroxides in ethers:

To 150 cc. of $2N$ sulphuric acid and 10 cc. of the ether, add 3 to 5 drops of 1 per cent ammonium molybdate[96] solution followed by 15 cc. of 10 per cent potassium iodide solution. After shaking thoroughly, and allowing to stand for 15 minutes, titrate the liberated iodine with $0.05N$ sodium thiosulphate, shaking well after each addition of reagent. As the end point is approached, add a few cc. of starch solution as indicator and titrate to disappearance of the blue color.

Arup[97] advises that peroxides be decomposed by treatment of the ether with silver oxide. If this is not feasible then incorporation of a small proportion of a fatty acid or vegetable oil practically eliminates all danger. MacCulloch[98] recommends inclusion of a short length of copper wire in the amber-colored bottles employed for storage of anesthetic ether.

ISOPROPYL HYDROPEROXIDE

This compound has been prepared by Medvedev and Alekseeva[99] by treatment of diisopropyl sulphate with hydrogen peroxide (30 per cent) in the presence of potassium hydroxide. A 50 per cent yield was secured. The substance is a mobile liquid with an irritating odor, boiling at 107-109°C. and exploding if heated to a high temperature. It is miscible in all proportions with water, alcohol and ether. Although relatively stable in quartz vessels, as well as in neutral or acid aqueous solutions, it decomposes rapidly in alkaline solutions with the formation of acetone. If manganous salts are present, the peroxide is oxidized by acid permanganate solution. It liberates iodine from hydrogen iodide quantitatively. In dry ether, the peroxide does not affect hydroquinone but in moist ether (or water) oxidizes it to quinhydrone. Interaction with barium hydroxide produces salts that are relatively stable in the dry state in air freed from carbon dioxide. A compound of formula $(CH_3)_2CHO{\cdot}O{\cdot}BaOCO_2H{\cdot}3H_2O$ was isolated. Treatment with terephthalyl chloride converted the hydroperoxide into the di-peroxide ester, $C_6H_4(CO{\cdot}O{\cdot}OCH(CH_3)_2)_2$. This latter compound melts at 59°C., and explodes on further heating. It decolorizes indigo very slowly and does not affect potassium iodide solutions. In faintly acid or neutral aqueous solution it is slowly converted into terephthalic acid and acetone.

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[94] E. C. Williams, *Chem. & Ind.*, 1936, 580; *Brit. Chem. Abs.* **A**, 1936, 1091.

[95] It has been pointed out that no explosions have been reported in the case of ethers boiling above 100°C., probably because the peroxides are slowly and safely decomposed at temperatures above the boiling point of water. See, *Ind. Eng. Chem., News Ed.*, 1936, **14**, 305.

[96] This substance acts as a catalyst for the liberation of iodine in the solution.

[97] P. S. Arup, *Chem. & Ind.*, 1936, 546; *Chem. Abs.*, 1936, **30**, 6563; *Brit. Chem. Abs.* **A**, 1936, 963.

[98] A. F. MacCulloch, *Chem. & Ind.*, 1936, 964.

[99] S. S. Medvedev and E. N. Alekseeva; *Ber.*, 1932, **65**, 133; *Chem. Abs.*, 1932, **26**, 2412; *Brit. Chem. Abs.* **A**, 1932, 363.

The normal propyl hydroperoxide was not isolated in pure form, but was separated as the salt $CH_3CH_2CH_2O_2BaCO_3H{\cdot}3H_2O$. With both normal hydroperoxide and terephthalate, decomposition (with liberation of propionaldehyde) was much more marked than with the corresponding isopropyl derivatives.

ISOPROPYL ALCOHOL AS AN ISOPROPYLATING AGENT

Direct alkylation of aromatic hydrocarbons by means of isopropyl alcohol under the influence of sulphuric acid as catalyst has been known for some years and probably proceeds through the intermediate formation of isopropyl sulphate. This mode of operation is cheaper than the Friedel-Crafts' synthesis and, in some cases, yields substances isomeric with those furnished by the latter method. Condensation of isopropyl alcohol with benzene in the presence of concentrated sulphuric acid has been studied by Kirrmann and Graves[100] who obtained monoisopropylbenzene (cumene), *p*-diisopropylbenzene b.p. 210°C. at 760 mm., 1,3,4-triisopropylbenzene, b.p. 244° at 760 mm. and 1,2,4,5-tetraisopropylbenzene, m.p. 118°C. and b.p. 169°C. at 70 mm. Under similar conditions, toluene and the alcohol yielded *p*-cymene and diisopropyltoluene, b.p. 98°-100°C. at 14 mm. By treating toluene with isopropyl alcohol in 80 per cent sulphuric acid, Meyer and Bernhauer[101] secured a 35 per cent yield of cymene. Subsequently, Desseigne[102] pointed out that much cymene remained in solution in the sulphuric acid as a sulphonic acid, which could be steam distilled at 160°C. to bring the yield up to 82 per cent. In addition, about 14 per cent of 2,4-diisopropyltoluene and 2,4,6-triisopropyltoluene were formed. It is interesting to note that both *o*- and *p*-cymenes were produced in the above experiments. Desseigne also showed that when 95 per cent sulphuric acid was used as catalyst, the yield of cymene was reduced to 38 per cent and that of higher substituted products increased to 47 per cent. Interaction of isopropyl alcohol with *p*-nitrotoluene in the presence of sulphuric acid yielded 4-nitro-*o*-cymene and 4-nitro-2,6-diisopropyltoluene.

Condensation between secondary alcohols and aromatic hydrocarbons can also be brought about by aluminum chloride. According to Tzukervanik and Tokareva[103] an intermediate compound is formed between the metallic chloride and the alcohol, this complex subsequently undergoing reaction with the aromatic hydrocarbon according to the scheme:

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[100] A. Kirrmann and M. Graves. *Bull. soc. chim.*, 1934, (5) 1, 1494; *Chem. Abs.*, 1935, **29**, 2516; *Brit. Chem. Abs.* **A**, 1935, 203.

[101] H. Meyer and K. Bernhauer, *Monatsh*, 1929, **53** and **54**, 721; *Chem. Abs.*, 1930, **24**, 346; *Brit. Chem. Abs.* **A**, 1929, 1441.

[102] G. Desseigne. *Bull. soc. chim.*, 1935, (5) **2**, 617; *Brit. Chem. Abs.* **A**, 1935, 739; *Chem. Abs.*, 1935, **29**, 3995. *Compt. rend.*, 1935, **200**, 466; *Brit. Chem. Abs.* **A**, 1935, 612; *Chem. Abs.*, 1935, **29**, *2927*.

[103] J. Tzukervanik and K. Tokareva. *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 764; *Brit. Chem. Abs.* **A**, 1936, 61; *Chem. Abs.*, 1936, **30**, 442.

$$ROH + AlCl_3 \longrightarrow HCl + AlCl_2{\cdot}OR$$

and

$$AlCl_2{\cdot}OR + C_6H_6 \longrightarrow AlCl_2{\cdot}OH + R{\cdot}C_6H_5$$

From benzene and isopropyl alcohol in the presence of aluminum chloride, these investigators obtained mono- and di-isopropylbenzenes. Under similar conditions *p*-cymene was the main reaction product from toluene. Huston and Hsieh[104] condensed isopropyl alcohol with 2 to 5 equivalents of benzene in the presence of 0.5 equivalent of aluminum chloride and secured small quantities of mono- and polyisopropylbenzenes. No appreciable reaction was observed between phenols and isopropyl alcohol under similar conditions.

It is reported that phenols may be alkylated by secondary alcohols (such as isopropyl) using a zinc chloride catalyst.[105] The reaction is effected in the presence of a volatile liquid of boiling point lower than about 130°C., for secondary and tertiary alcohols, for which this method is especially suited. Solvent, phenol and alcohol are added to the dissolved zinc chloride. The mixture is then heated under reflux. After cooling, the upper layer (carrying the alkylated phenol) is washed with water to remove zinc chloride and purified by vacuum distillation. Addition of a small amount of a 1 per cent sodium hydroxide solution to the wash water has been found expedient in extracting the last traces of the catalyst.

The rearrangement of complex isopropyl aromatic ethers has been carried out by means of boron trifluoride.[106] For example, the addition of boron trifluoride gas to isopropyl phenyl ether, with no external cooling, resulted in a vigorous reaction. From 250 grams of the ether were obtained the following substances:

Phenols

2-isopropyl phenol	34 grams
2,4-diisopropyl phenol	44 "
2,4,6-triisopropyl phenol	28 "
phenol	90 "

Ethers

2-isopropylphenyl isopropyl ether	trace
2,4-diisopropylphenyl isopropyl ether	32 grams
2,4,6-triisopropylphenyl isopropyl ether	12 grams
phenylisopropyl ether	trace

Similar treatment of the isopropyl *o*-, *m*-, and *p*-cresyl ethers led to the generation of corresponding alkylated phenols or phenol ethers.

Conductivity measurements of the system phenol-boron fluoride indicated compound formation corresponding to $BF_3{\cdot}2C_6H_5OH$. A similar substance has been shown to result from an equimolar addition of boron fluoride to an alkyl phenyl ether. These intermediate reactions were considered by Sowa, Hinton and Nieuwland to explain the numerous inter- and intra-molecular changes reported. It was also stated that nearly all the compounds described in their work were likewise prepared from propene and the appropriate phenol.[107]

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[104] R. C. Huston and T. Y. Hsieh, *J.A.C.S.*, 1936, **58**, 439; *Chem. Abs.*, 1936, **30**, 2939; *Brit. Chem. Abs.* **A**, 1936, 602.

[105] H. Langwell and E. E. Connolly, British P. 425,373, 1935, addn. to 424,506, to British Industrial Solvents, Ltd.; *Brit. Chem. Abs.* **B**, 1935, 443; *Chem. Abs.*, 1935, **29**, 5458, 4376.

[106] F. J. Sowa, H. D. Hinton and J. A. Nieuwland, *J.A.C.S.*, 1933, **55**, 3402; *Chem. Abs.*, 1933, **27**, 4785; *Brit. Chem. Abs.* **A**, 1933, 1045.

[107] For a discussion of the interaction between olefins and phenols, see Chapter 24.

Continuing this study of boron fluoride-organic reactions, Sowa, Hennion and Nieuwland[108] accomplished the alkylation of phenol with propyl alcohol. Identical compounds were obtained from both the normal and the iso-forms of propanol. No *n*-propyl phenyl ether was found in the products of reaction but only the derivatives containing the isopropyl radical (see Table 95.)

TABLE 95.—*Condensations of Propyl Alcohols with Phenol.*

Product	Yield in Grams per Mole of Phenol From Isopropyl Alcohol	 From *n*-Propyl Alcohol
2,4-Diisopropylphenyl isopropyl ether	11	13
2-Isopropyl phenol	28	32
4-Isopropyl phenol	20	16

Comparison of the physical properties of these substances showed them to be identical with those reported in previous work.[109] The results were considered to indicate that such condensations take place by means of intermediate-olefin formation followed by interaction with phenol.

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[108] F. J. Sowa, G. F. Hennion and J. A. Nieuwland, *J.A.C.S.*, 1935, *57*, *709*; *Brit. Chem. Abs.* **A**, 1935, 744; *Chem. Abs.*, 1935, **29**, 3321.

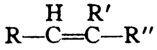
[109] F. J. Sowa, H. D. Hinton and J. A. Nieuwland, *J.A.C.S.*, 1933, **55**, 3402; *Chem. Abs.*, 1933, **27**, 4785; *Brit. Chem. Abs.* **A**, 1933, 1045.

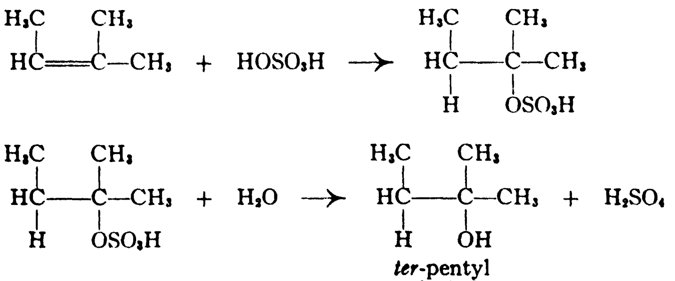
Chapter 16

Production of Higher Secondary and Tertiary Alcohols. Reactions of Sulphuric Acid with Higher Homologues of Ethylene and Propene

The reaction between sulphuric acid and the higher monolefins differs in a real and important degree from that between this acid and the lower monolefins, e.g., propene or ethylene. This is technically important because of the difficulty in effecting separation (by fractional distillation) of isomeric olefins (e.g., butene and isobutene) or of olefins and the corresponding diolefins. Dilute sulphuric acid should be employed to reduce its polymerizing action, particularly on hydrocarbons of the isobutene type. Furthermore, if diolefins are present these may undergo considerable co-polymerization with monolefins, thus promoting undesirable side reactions rather than alcohol formation.

There are three general classes of higher olefins, each reacting with sulphuric acid in a different manner and at different reaction velocities.[1] These may be characterized as follows:

> Class I. The highly reactive tertiary olefins which contain the grouping:
>
> 
>
> $$R-\overset{H}{C}=\overset{R'}{C}-R''$$
>
> Where R′ and R″ are alkyl groups, and R represents an alkyl group or hydrogen atom. These compounds react and dissolve readily in sulphuric acid of 60 to 70 per cent concentration, but polymerize in the presence of acid of higher concentration. The product of sulphation and subsequent hydrolysis is a tertiary alcohol. Trimethylethylene is a typical example of this class of hydrocarbon:



$$\overset{H_3C}{HC}=\overset{CH_3}{C}-CH_3 + HOSO_3H \longrightarrow \underset{H}{\overset{H_3C}{HC}}-\underset{OSO_3H}{\overset{CH_3}{C}}-CH_3$$

$$\underset{H}{\overset{H_3C}{HC}}-\underset{OSO_3H}{\overset{CH_3}{C}}-CH_3 + H_2O \longrightarrow \underset{H}{\overset{H_3C}{HC}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 + H_2SO_4$$

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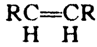
[1] J. F. Norris and H. S. Davis, *J.S.C.I.*, 1929, **48**, 70T; *Brit. Chem. Abs.* **B**, 1929, 463; *Chem. Abs.*, 1929, **23**, 2932.

Class II. These are typified by the grouping:

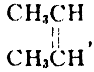


$$\begin{array}{c}RC{=}CR' \\ H\quad H\end{array}$$

wherein R or R′ may be a hydrogen atom or an alkyl group. Such hydrocarbons are less reactive, both to sulphation and to polymerization, than are the corresponding tertiary compounds. Sulphation of these olefins requires acid of 75 to 85 per cent concentration, and little polymerization occurs. The products consist of sulphuric acid esters of secondary alcohols. This class is represented by *n*-alkenes, such as *n*-butene and *n*-pentene.

Class III. This very limited class is, at present, known to be represented by only one compound, isopropyl-ethylene. The hydrocarbon yields practically no sulphuric acid esters of the corresponding alcohol, but only polymerization products, when treated with acid of concentration higher than that required to react with the tertiary compounds of Class I.

Reactions of the Butenes. Of the four isomeric butenes (butene-2 existing as cis- and trans-isomers), isobutene is a typical tertiary olefin of Class I. This hydrocarbon dissolves smoothly in sulphuric acid of about 65 per cent concentration, and the resulting solution, on hydrolysis and neutralization, yields *ter*-butyl alcohol exclusively. If the acid solution is heated without dilution, polymers of isobutene (such as diisobutylene) can be recovered in good yield. The latter are useful as solvents, and in the production of high-octane motor fuels. Similarly, absorption of isobutene in sulphuric acid of concentration materially above 65 per cent yields polymer hydrocarbons at low temperatures.[2] According to Brooks,[3] isobutene can be selectively removed from a C_4 fraction, containing in addition *n*-butene and butadiene, by absorption in 65 per cent sulphuric acid at 10° to 15°C. without polymerization of the diolefin present. Mezhebovskaya[4] reported a study of a fraction, consisting largely of butenes, obtained by absorption of cracking gas on charcoal. This investigator observed that production of *ter*-butyl alcohol was maximal when the temperature of sulphation was −10° to +10°C., and the sulphuric acid concentration 75 to 65 per cent. Lower temperatures, and more efficient cooling, was needed when higher acid concentrations were used.

The sulphation and hydrolysis of butene-1 yields butanol-2, or *sec*-butyl alcohol, as does the similar treatment of either of the two isomeric forms of butene-2, i.e., *cis*-butene-2,  $\begin{array}{c}CH_3CH \\ \| \\ CH_3CH\end{array}$, and *trans*-butene-2, $\begin{array}{c}CH_3CH \\ \| \\ CHCH_3\end{array}$. In this conversion, however, acid of concentration ranging from 75 to 85 per cent is needed, although even stronger acid (90 to 100 per cent) has been suggested, when efficient refrigeration is employed.[5] With high acid concentrations, however, temperature regulation becomes progressively more difficult, while polymerization and side reactions increase in prominence. The normal butenes are rapidly sulphated in the liquid phase by 70 to 75 per cent sulphuric acid at 20° to 30°C., with little or no polymerization. Somewhat higher acid concentrations are advantageous, however, when treating liquid butenes diluted with relatively large proportions of saturated hydrocarbons, such as butane or isobutane. Under the conditions employed in the sulphation of normal butenes any butadiene present undergoes complete polymerization to high-boiling, unsaturated oils. These appear to result from the copolymerization of equimolar proportions of butadiene and *n*-butene.[6]

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[2] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[3] B. T. Brooks, *Ind. Eng. Chem.*, 1935, **27**, 278; *J. Inst. Pet. Tech.*, 1935, **21**, 226A; *Chem. Abs.*, 1935, **29**, 2700.

[4] E. Mezhebovskaya, *Azer. Neft. Khoz.*, **1933**, No. 6-7, 53; *Chem. Abs.*, 1934, **28**, 7489; *Brit. Chem. Abs.* **B**, 1935, 329.

[5] W. Engs and R. Z. Moravec, U. S. P. 1,912,695, June 6, 1933; *Brit. Chem. Abs.* **B**, 1934, 186; *Chem. Abs.*, 1933, **27**, 4240. U. S. P. 1,938,177, Dec. 5, 1933; *Brit. Chem. Abs.* **B**, 1934, 824; *Chem. Abs.*, 1934, **28**, 1048. U. S. P. 1,967,399, July 24, 1934; *Brit. Chem. Abs.* **B**, 1935, 618; *Chem. Abs.*, 1934, **28**, 5832. All patents to Shell Development Co.

Pure normal butenes, on sulphation and hydrolysis, yield about 80 per cent of the theoretical quantity of butanol-2. Brooks[7] states that when the acid liquors are diluted with ice water, some 20 to 24 per cent of the alcohol obtainable is liberated as such. The remainder is secured only after heating the diluted liquor

Certain acid-soluble salts act catalytically to accelerate absorption of the olefins in sulphuric acid.[8] Silver sulphate, for instance, has a very pronounced effect on the absorption of ethylene, though the effect is progressively less with the heavier olefins. Vanadium, uranium and tungsten were much less effective. Markovich, Moor and Dement'eva[9] studied the use of a number of substances, including metallic salts and certain organic compounds. They point out that there are two phases of the problem to be considered; physical solution of the unchanged, unreacted hydrocarbon in the sulphuric acid during which the acid acts solely in the role of a solvent, and the subsequent chemical reaction of the acid and olefin. A few compounds insoluble in sulphuric acid were found to accelerate solution, without effecting chemical reaction. Although over thirty different compounds were investigated, ranging from the light alkali metals to the heavy metals such as uranium, it was found that silver salts (reacting to form silver sulphate) were most active. Some of the salts investigated retarded rather than accelerated absorption of the olefins.

The Pentenes. Trimethylethylene and unsymmetrical methylethylethylene are the five-carbon representatives of the Class I olefins noted above. These hydrocarbons can be converted almost quantitatively into *ter*-amyl alcohol by sulphation with 60 to 70 per cent sulphuric acid and subsequent hydrolysis. More concentrated acid results in considerable polymerization of the olefin.

Pentene-1 and pentene-2 are typical representatives of Class II olefins, giving practically theoretical yields of the secondary alcohols when treated with 82 to 90 per cent sulphuric acid (at 15° to 20°C.), followed by hydrolysis. Brooks,[10] however, has shown that pentene-1 yields only the acid esters of pentanol-2, that is, no *n*-amyl esters, when treated with 84 per cent sulphuric acid, even in the presence of a catalyst (hydrogen peroxide and benzoyl peroxide).[11] Under similar conditions, pentene-2 and 80 per cent sulphuric acid at 20°C. furnished a mixture of the esters of both pentanol-2 and pentanol-3, in ratio of 65 per cent of the former to 35 per cent of the latter. Thus, although the sulphate group attaches at either end of the double bond of pentene-2, it is directed to the more central carbon atom in pentene-1.

The pentene isopropylethylene is unique in that it forms mainly polymers when treated with 80 to 90 per cent sulphuric acid at 15 to 20°C. Practically no sulphated products result from this treatment, and lower concentrations of acid react only very slowly with the hydrocarbon. Brooks[12] suggests that the unique behavior is due to the formation of a tertiary alkyl sulphate rather than the secondary compound which might be expected. But since a high concentration of acid (80 to 96 per cent) is required to bring about reaction, the product when formed reacts as do other tertiary alkyl sulphates in acid of such concentration, and polymerizes rapidly. Brooks states that relatively large quantities of unsaturated oils arise from polymerization during the sulphuric acid treatment of pentene fractions from cracked petroleum. He believes the change is a manifestation of the tendency of certain olefins to copolymerize with other olefins which latter would not by themselves polymerize under the conditions that obtain.

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[6] B. T. Brooks, U. S. P. 1,894,661, Jan. 17, 1933, to Petroleum Chemical Corp.; *Chem. Abs.*, 1933, **27**, 2572; *Brit. Chem. Abs.* **B**, 1933, 903.

[7] B. T. Brooks, *Ind. Eng. Chem.*, 1935, **27**, 278; *J. Inst. Pet. Tech.*, 1935, **21**, 226A; *Chem. Abs.*, 1935, **29**, 2700.

[8] V. V. Pigulevskii, *Trans. VI Mendeleev Congr. Theoret. Applied Chem. 1932*, 1935, **2**, Pt. 1, 711; *Chem. Abs.*, 1936, **30**, 2734.

[9] M. B. Markovich, V. G. Moor and M. I. Dement'eva, *Materials on Cracking and Chem. Treatment of Products Obtained, Goskhimtekhizdat, (Leningrad)*, **1933**, No. 1, 77; *Chem. Abs.*, 1935, **29**, 2059.

[10] B. T. Brooks, *J.A.C.S.*, 1934, **56**, 1998; *Chem. Abs.*, 1934, **28**, 6697; *Brit. Chem. Abs.* **A**, 1934, 1198; *J. Inst. Pet. Tech.*, 1934, **20**, 566A.

[11] It has been found that peroxides exert a directive action in the combination of the halide acids with olefins, leading to the formation of primary alkyl halides. This is discussed in Chapter 12.

Pipik and Mezhebovskaya[13] conducted an investigation of the preparation of amyl alcohols from the pentene fractions of various cracked gasolines. As sulphating agents they employed sulphuric acid ranging in concentration from 75 to 85 per cent. Secondary amyl alcohols constituted the main products. The highest alcohol yields were found to result from treatment of 1 part of the amylene fraction with 1 to 1.3 parts of 75 per cent acid, or 0.75 part of 80 per cent acid. The light ends of a liquid-phase cracked gasoline furnished about 5.5 per cent by weight of amyl alcohols. A similar distillate obtained by vapor-phase cracking at 680°C. gave about 6 per cent of the alcohols. Pipik[14] subsequently observed that the hydrocarbons (boiling at about 55°C.) separated in the rectification of the amyl alcohols contained amylenes which, after treatment with additional acid, furnished more secondary amyl alcohols. It was noted that this amylene fraction contained an activator and was thereby rendered chemically active. The activated condition was considered to be further indicated by reaction with sulphur dioxide, which resembled that exhibited by the hydrocarbons of the isoprene series. The activator, however, could not be isolated.

Nazarov[15] reported a two-stage sulphation for preparing the pentyl alcohols from hydrocarbon fractions boiling below 30°C., between 30° and 40°C. and between 40° and 45°C. The material was subjected to a primary sulphation with 75 per cent sulphuric acid at 0° to —10°C. The product of this treatment was principally the tertiary alcohol 2-methylbutanol-2. The second treatment with 80 per cent acid at 20°C. yielded largely secondary pentyl alcohol, pentanol-2. These alcohols represented 39.3 per cent of the hydrocarbon undergoing reaction.

The Hexenes. The available data on the sulphation of the various hexenes is less complete than that concerning the lower members of the series. However, the tertiary olefins, tetramethylethylene and 2-methylpentene-1, are known to furnish the corresponding tertiary alcohols, 1,1,2-trimethylpropanol-1 and 2,2-dimethylbutanol-1, respectively, when sulphated with 75 to 80 per cent acid and subsequently hydrolyzed. Hexene-1 readily reacts with 85 per cent acid to yield (after hydrolysis) hexanol-2. Similarly, hexene-2 gives a mixture of 75 per cent of hexanol-2 and 23 per cent hexanol-3. The behavior of other hexenes towards sulphuric acid is still unknown. A gasoline fraction (boiling from 55° to 75°C.) was redistilled by Nazarov and Remiz[16] to obtain the fraction corresponding to the hexenes. It was found that there was a high benzene content in the 75° to 80°C. cut, and the investigators recommended that the lower boiling portion (from 55° to 75°C.) be used. On treating the latter first with 75 per cent sulphuric acid at 0°C. and then with 85 per cent acid at 5° to 10°C., followed by hydrolysis of the acid liquor, one tertiary alcohol, 2-methylpentanol-2, was recovered in 4.5 per cent yield, and the secondary alcohol hexanol-3 in 14.4 per cent yield (based on the total unsaturated hydrocarbons in the original fraction).

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[12] B. T. Brooks, *Ind. Eng. Chem.*, 1935, **27**, 282; *Chem. Abs.*, 1935, **29**, 2700; *Brit. Chem. Abs.* B, 1935, 536; *J. Inst. Pet. Tech.*, 1935, 21, 226A.

[13] O. Pipik and E. Mezhebovskaya, *Azer. Neft. Khoz.*, 1933, No. 6-7, 56; *Chem. Abs.*, 1934, **28**, 7504.

[14] O. Pipik, *Azer. Neft. Khoz.*, 1934, No. 10, 86; *Chem. Abs.*, 1935, **29**, 5808; *Brit. Chem. Abs.* B, 1936, 536.

[15] S. A. Nazarov, *Materials on Cracking and Chem. Treatment of Products Obtained, Goskhimtekhizdat (Leningrad)*, 1933, No. 1, 102; *Chem. Abs.*, 1935, **29**, 2719; *Brit. Chem. Abs.* B, 1935, 1031.

[16] S. A. Nazarov and E. K. Remiz, *Materials on Cracking and Chem. Treatment of Products Obtained, Khimteoret, (Leningrad)*, 1935, No. 2, 172; *Chem. Abs.*, 1935, **29**, 6033; *Brit. Chem. Abs.* B, 1936, 1188.

SEVERAL PROCESSES FOR THE SULPHATION OF OLEFINS

Tertiary Olefins. It is not practicable to separate by distillation[17] tertiary and secondary unsaturates occurring in the mixtures available for technical processes. However, advantage may be taken of the considerable differential in their reactivity with respect to sulphuric acid of various concentrations and a fairly complete separation may be secured in this way. The higher reactivity of the tertiary olefins makes possible a preferential conversion of these hydrocarbons to the sulphuric esters of the corresponding alcohols, while the less reactive secondary olefins remain substantially unaffected.[18] The residual olefins may then be treated with a more concentrated acid for the production of secondary alcohols. In carrying out this two-stage process, diolefins (such as butadiene) must be removed before the second step, otherwise co-polymerization of these with secondary olefins occurs. Perkins and Davies[19] prefer to separate the diolefins prior to the first sulphation treatment. A cracked hydrocarbon fraction consisting of four- and five-carbon atom chains, from which the diolefins had first been recovered, was treated with 55 to 65 per cent sulphuric acid at 10° to 35°C. to form a tertiary sulphate liquor, from which the corresponding alcohols could be recovered by hydrolysis. The hydrocarbon residue from this step was subsequently treated with 75 per cent sulphuric acid at a temperature below 20°C. to form a secondary sulphate liquor.

LeBaron[20] has described a procedure for sulphation of the butene fraction (in the liquid phase) separated from cracking gas. Sulphuric acid of 50 to 60 per cent strength is employed. The aqueous acid, containing tertiary butyl acid sulphate, is then removed and the residual liquid olefins treated with a second quantity of sulphuric acid of 65 to 70 per cent concentration. Brooks[21] proposes

[17] Although the most important technical source of olefinic material for the synthesis of alcohols is, perhaps, the unsaturated gases derived from cracking operations, other raw materials have been suggested. It has been reported, (S. V. Lebedev, V. P. Krause, I. A. Volzhinskii, Y. O. Gorin and O. M. Neimark, *Trudui Gosudarst. Opuit. Zavoda Sintct. Kauchuka Litera B. III., Synthetic Rubber,* **1934**, 68; *Chem. Abs.*, 1936, **30**, 4811.) that pseudobutene (butene-2) is obtained as a by-product in the preparation of synthetic rubber from bivinyl, and can be recovered by ordinary or vacuum distillation from the polymerizate. The investigators recovered secondary butyl alcohol in 83 per cent yield by treating the butene in the liquid phase with 75 per cent sulphuric acid. The unpurified gases from the polymerized product contain some bivinyl (up to 3 per cent) which could not be removed by treatment with sulphuric acid. An additional polymerization with metallic sodium did remove it, however. S. E. Campbell (U. S. P. 1.938.094, Dec. 5, 1933; *Brit. Chem. Abs.* **B**, 1934, 918; *Chem. Abs.*, 1934, **28**, 1180) has pointed out that hydrocarbon distillates may be decolorized by treating the material in towers successively with dilute sulphuric acid, alkali solution, concentrated acid, and a final water wash. Alcohols may be recovered by hydrolysis of the concentrated sulphuric acid liquors after dilution. The residual dilute acid from this latter step serves as the dilute acid of the first scrubbing tower.

[18] G. H. van de Griendt and W. Engs, U. S. P. 2,060,143, Nov. 10, 1936; *Chem. Abs.*, 1937, **31**, 416. British P. 453,073, 1936, to N. V. de Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1937, **31**, 1036; *Brit. Chem. Abs.* **B**, 1936, 1141; *J. Inst. Pet. Tech.*, 1936, **22**, 515A. French P. 792,105, 1935; *Chem. Abs.*, 1936, **30**, 4175. See also W. H. Groombridge, British P. 415,766, 1934, to British Celanese, Ltd.; *Chem. Abs.*, 1935, **29**, 811; *J. Inst. Pet. Tech.*, 1934, **20**, 584A; *Brit. Chem. Abs.* **B**, 1934, 952.

[19] G. A. Perkins and J. A. Davies, Canadian P. 350.409, 1935, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, **29**, 5127.

[20] R. F. LeBaron, U. S. P. 2,028,226, Jan. 21, 1936, to Standard Alcohol Co.; *Chem. Abs.*, 1936, **30**, 1805.

[21] B. T. Brooks, U. S. P. 1,970,687, Aug. 21, 1934, to Standard Alcohol Co.; *Chem. Abs.*, 1934, **28**, 6157; *Brit. Chem. Abs.* **B**, 1935, 715.

to treat liquid butenes under superatmospheric pressure with about 63 per cent acid, to form an acid mixture containing monobutyl hydrogen sulphate. Water is then added and unreacted *n*-butenes separated from the resulting mixture Clark and Worster[22] suggested a countercurrent method of treating amylene fractions, with sulphuric acid of about 61 per cent concentration, to selectively react the tertiary hydrocarbons. The acid thus prepared is hydrolyzed afterwards by stirring with water and cooling below 30°C.

The removal of tertiary olefins and other highly reactive unsaturated hydrocarbons from their admixtures with secondary olefins may be effected by other means than sulphation. Polymerization may be carried out under such conditions as to convert these more reactive substances, without appreciable change of the secondary olefinic compounds. According to Engs and Moravec[23] the raw material containing both secondary and tertiary olefins may be treated with an acid of such strength as to bring about a substantially complete polymerization of the more reactive tertiary compounds, yet not strong enough (at the temperature employed) to materially polymerize the secondary compounds. The investigators point out, however, that this method may lead to an incomplete sulphation of the secondary olefins, thus reducing the yield of corresponding alcohols. They propose, therefore, to carry out the reaction in two separate steps. A butane-butene hydrocarbon fraction, for instance, may be first contacted (countercurrently) with 60 to 70 per cent sulphuric acid at 50°C. Under these conditions, isobutene is polymerized, while the butene-1 and butene-2 present are hardly affected. From this reactor, the fluid, now containing isobutene polymers, *n*-butenes, butane and isobutane is passed into a second reactor where it is treated with 90 to 100 per cent sulphuric acid, at a temperature of 15°C. In this latter operation sulphation of straight-chain butenes is effected. Above this temperature, it is reported, undesirable side reactions occur.

Hydrolysis and distillation of the resulting aqueous layer yield the secondary alcohol. If the polymers of isobutene have been attacked by the concentrated sulphuric acid in the second reactor, they revert to the original polymer under subsequent treatment and are readily separated. As an alternative procedure it is suggested[24] that tertiary olefins be selectively absorbed in sulphuric or phosphoric acid, which is removed and heated to approximately 80°C., causing polymerization of the dissolved hydrocarbon. The polymers may be separated from the acid, which is returned to the system for reuse. Sulphuric acid of 65 per cent concentration at a temperature of 55°C. may be employed in the absorbing chamber of this process.[25]

It has also been reported[26] that the presence of a bivalent metal sulphate in the sulphuric acid used in absorbing the olefinic material makes it possible to recover the tertiary olefins. These hydrocarbons dissolve readily in such a solution but may be released and recovered in a substantially pure condition on heating the liquid. Presumably polymerization is minimized by use of the soluble metal sulphate catalyst.

For the production of *ter*-butyl alcohol, Huyser and Van Melsen[27] propose to absorb the corresponding olefin in acid of concentration sufficiently low to prevent formation of any appreciable amount of polymerization products. They suggest the use of one hydrogen equivalent of acid (e.g., 65 per cent sulphuric acid) per mole of isobutene. It has been reported that the polymerization of olefins in the presence of sulphuric acid is inhibited by the addition of cyanides or complex cyanides of platinum, copper, iron, cobalt, nickel or silver.[28] The salts of metals of the 8th group of the periodic table, e.g., nickelous cyanide, $Ni(CN)_2$, are said to facilitate absorption of the olefinic material in the acid.[29] Cuprous salts have also been suggested for the same purpose.

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[22] L. H. Clark and F. J. Worster, U. S. P. 2,006,942, July 2, 1935, to Sharples Solvents Corp.; *Chem. Abs.*, 1935, **29**, 5457; *Brit. Chem. Abs.* B, 1936, 919.

[23] W. Engs and R. Z. Moravec, U. S. P. 1,938,177, Dec. 5, 1933, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 1048; *Brit. Chem. Abs.* B, 1934, 824.

[24] W. Engs and R. Moravec, U. S. P. 2,007,159, July 9, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 5456; *J. Inst. Pet. Tech.*, 1936, **22**, 53A.

[25] W. Engs and R. Moravec, U. S. P. 2,007,160, July 9, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 5456; *Brit. Chem. Abs.* B, 1936, 632.

[26] R. M. Deanesly and W. Engs, Canadian P. 349,628, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 4020.

[27] H. W. Huyser and J. A. van Melsen, U. S. P. 2,012,787, Aug. 27, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 6903. See also Dutch P. 30,237, 1933; *Chem. Abs.*, 1933, **27**,

In sulphating a mixture of olefins and diolefins derived from cracking processes, Brooks[30] suggests a fraction containing mainly butenes and butadiene. Diolefins are first removed (without polymerization) by contact with a slurry of cuprous chloride in an aqueous ammonium chloride solution. The remaining mixture is then freed of tertiary olefins with 60-65 per cent sulphuric acid at 25°C. or lower. Subsequent treatment with 65-75 per cent acid at 35-60°C. removes the normal butenes, and the propene remaining is then absorbed by 80-85 per cent acid at 20-40°C. If any ethylene remains in the unabsorbed portion, this may be sulphated with 85-95 per cent acid at 30-100°C.

According to some investigators,[31] solution of an olefin in aqueous sulphuric acid can be effected to produce a liquor containing most of the absorbed olefin in the form of the free alcohol, which can be separated by solvent extraction. For example, isobutene may be absorbed in 58 per cent sulphuric acid (containing 0.5 per cent of cuprous oxide) at 50°C. under atmospheric pressure. The resulting liquor (possessing 250 grams of free *ter*-butyl alcohol per liter) is extracted with one and a half times its volume of cresol. On extraction, the solvent is said to contain 100 grams of alcohol per liter, while the acid liquor contains an equal concentration of the alcohol. After washing with water to remove entrained acid, alcohol and solvent are separated by fractionation and the latter reused. This process is said to be advantageous in that it obviates the necessity of diluting and reconcentrating the sulphuric acid. The same type of treatment is reported efficacious with trimethylethylene, using 50 per cent sulphuric acid in this case, and ethylphenol as the extracting solvent. The extract finally contains upwards of 20 per cent of *ter*-amyl alcohol.

Secondary Olefins. In converting butenes and pentenes into sulphuric acid esters of the corresponding alcohols, the usual practice is to contact the olefin (often in the liquid phase) under slight pressure with sulphuric acid of the requisite concentration. Careful control of temperature is also necessary. Tertiary olefins and diolefins are removed prior to the sulphation, since undesirable side reactions and polymerizations tend to occur if they are present. Depending on temperature, acid concentration, and the relative proportions of olefin material to acid employed, secondary olefins may be converted to mono- or di-sulphates, or into polymerization products. At normal temperatures, acid concentrations of approximately 80 per cent appear to be best for the production of alcohols, but stronger acid may be used under low-temperature conditions. Employment of

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5756. French P. 716,046, 1931; *Chem. Abs.*, 1932, **26**, 1946. German P. 590,483, 1934; *Chem. Abs.*, 1934, **28**, 2020. All patents to Bataafsche Petroleum Maatschappij.

[28] Dutch P. 31,611, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 2368.

[29] German P. 598,538, 1930, to Bataafsche Petroleum Maatschappij; *J. Inst. Pet. Tech.*, 1934, **20**, 542A; *Chem. Abs.*, 1934, **28**, 5831. See also A. J. van Peski, U. S. P. 1,944,622, Jan. 23, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 2012.

[30] B. T. Brooks, U. S. P. 2,058,851, Oct. 27, 1936, to Standard Alcohol Co.; *Chem. Abs.*, 1937, **31**, 109.

[31] French P. 799,704, 1936, to Usines de Melle; *Chem. Abs.*, 1936, **30**, 8240. R. M. Deanesly, U. S. P. 2,042,212, May 26, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 4870.

stronger acid, however, makes the accurate control of temperature more difficult and at the same time more important if polymerization is to be minimized. Perkins and Davies[32] produced secondary alkyl sulphate liquors by treating a mixture of four- and five-carbon atom olefins, previously freed of diolefins and tertiary olefins, with 75 per cent sulphuric acid at temperatures below 20°C. The *n*-butenes (in the butane fraction of cracking gas) may be sulphated in the liquid phase with sulphuric acid of 65 to 70 per cent strength according to LeBaron.[33] Iso-olefins are first removed by treating the fraction with 50 to 60 per cent acid. Brooks[34] suggests that sulphation reactions may be controlled effectively by adding the liquid olefin to the sulphuric acid in such manner that the ratio of acid to olefin is maintained in excess of that required to form the monoalkyl sulphate.

Dialkyl sulphates may be prepared by treating *n*-olefins of four or more carbon atoms with 90 to 100 per cent acid, after the iso-olefins have been removed with 65 to 70 per cent sulphuric acid. For example, dibutyl sulphate may be obtained by the action of sulphuric acid (one mole) on liquid butene (two moles).[35] Concentrated acid of 90 to 100 per cent strength has also been used by Engs and Moravec[36] at temperatures below 47°C., but in this case, approximately equivalent proportions of the reactants were employed. The secondary alcohols are obtained by dilution of the alkyl sulphate solution to 25 or 35 per cent acidity.

It has been reported that metal cyanides present in 90 per cent acid not only act to inhibit polymerization of absorbed olefins but also do not promote esterification. The complex resulting from the interaction of unsaturated hydrocarbons, cyanides and acid is said to have a pronounced catalytic effect in facilitating the solution of further olefinic material. The strong acid solution containing the complex, after dilution, may be used in absorbing further quantities of hydrocarbons.[37] A catalyst composed of a compound of a metal of group VIII, such as ferrocyanic acid, has been proposed for absorption of cyclic unsaturated hydrocarbons, such as cyclohexene, in 80 per cent sulphuric acid. Subsequent hydrolysis furnishes the cyclic alcohol.[38]

Davis and Francis[39] report that heating (at 84 to 95°C. under 500 pounds per square inch pressure) a readily sulphated olefin, such as propene or butene, with an aqueous solution of the sulphuric acid ester of an olefin more difficult to sulphate (e.g., ethyl sulphate) results in a mixture of ethyl alcohol and the alcohol corresponding to the olefin introduced into the solution.

One of the main difficulties associated with the reaction between the higher olefins and sulphuric acid, of concentration greater than 90 per cent, is that considerable heat is evolved. This means that temperature regulation becomes important, if polymerization is to be controlled, since a rise in temperature brings about the formation of increasing proportions of polymers. For this reason, reaction is usually carried out in the liquid phase (and under pressure, if necessary) in vessels equipped with agitating devices and internal cooling coils. However, Deanesly[40] takes advantage of the volatility of the hydrocarbons being sulphated to regulate the temperature. He proposes that an olefin-containing mixture and sulphuric acid be intimately contacted in a packed column. The heat of reaction vaporizes a portion of the hydrocarbon, and these gases are collected, condensed, and reintroduced at a higher point in the column. Sufficient hydrocarbon is present, however, to insure that there shall be liquid material in the reaction zone at all times. Accurate temperature control is possible in this way, it is said. Alternatively, Young[41] produces alkyl sulphates by forcing a liquefied olefin and 75 to 100 per cent sulphuric acid at temperatures below 40°C. countercurrently through a flow path of restricted cross section. The length of the path is such that reaction will be substantially complete within it. The suggested form of the apparatus consists of a bank of relatively small-bore tubes immersed in a cooling medium. Kramer,[42] on the other hand, reported a method of control of the temperature of reaction by allowing interaction to take place in a comparatively large mass of fluid. The latter is recirculated, and cooled below the desired maximum temperature, so that the heat generated during interaction shall not be great enough to unduly increase the liquid's temperature. The fluid may consist of an inert liquid, one of the reacting substances present in great excess, or a by-product of the reaction. In the latter case, the substance employed is so chosen that it may be readily separated.

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[32] G. A. Perkins and J. A. Davies, Canadian P. 350.409, 1935, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, **29**, 5127.

[33] R. F. LeBaron, U. S. P. 2,028.226, Jan. 21, 1936, to Standard Alcohol Co.; *Chem. Abs.*, 1936, **30**, 1805; *Brit. Chem. Abs.* **B**, 1937, 117.

[34] B. T. Brooks, U. S. P. 1,940,073, Dec. 19, 1933, to Standard Alcohol Co.; *Chem. Abs.*, 1934, **28**, 1354; *Chem. Zentr.*, 1934, 1, 2488.

[35] German P. 577,947, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 489.

[36] W. Engs and R. Moravec, U. S. P. 1.912,695, June 6, 1933, to Shell Development Co.; *Brit. Chem. Abs.* **B**, 1934, 186; *Chem. Abs.*, 1933, **27**, 4240. See also Canadian P. 325,023, 1932, to Shell Development Co.; *Chem. Abs.*, 1932, **26**, 5309; U. S. P. 1. 967.399, July 24, 1934, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 5832; *Brit. Chem. Abs.* **B**, 1935, 618.

[37] Dutch P. 32.446, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 5076.

[38] A. J. van Peski, U. S. P. 1,948,891, Feb. 27, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 2723.

[39] H. S. Davis and A. W. Francis, U. S. P. 2,047,194, July 14, 1936, to Socony-Vacuum Oil Co.; *Chem. Abs.*, 1936, **30**, 6006.

LeBaron[43] described a method which involved a series of steps, each individually controlled as to acid concentration and temperature. The raw hydrocarbon material is mixed with sulphuric acid of relatively low concentration and the acid reaction product separated from the unreacted hydrocarbon. The unchanged olefinic material then passes to a second zone, where more concentrated sulphuric acid is contacted with it. The hydrocarbon and acid in each zone are reacted while flowing in a continuously moving stream, the temperature of which is controlled to prevent undesired side-reactions, while permitting sulphation of the olefin. A number of these successive reactions may be used, the hydrocarbon meeting successively stronger acid in each.

Markovich and Pigulevskii[44] sulphate the normally gaseous products of pyrolysis by adding sulphuric acid in batches to the hydrocarbon material, which is maintained in the liquid state by the application of pressure, or by solution in higher hydrocarbon fractions. The process temperature is allowed to rise during the reaction from 0°C. to a final value of about 60°C.

The reaction between liquid olefins and sulphonic acids, such as benzenesulphonic acid, may be employed as an intermediate step in the formation of the alkyl esters of organic acids.[45] The sulphonic acid and the olefin are reacted with agitation at a temperature from 25° to 100°C., and the resulting alkyl sulphonate ester is heated with an appropriate organic acid (e.g., acetic acid). Alternatively, the olefin and the organic acid may be directly heated together in the presence of the benzene sulphonic acid, the two reactions proceeding simultaneously.

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[40] R. M. Deanesly, U. S. P. 1,955,873, April 24, 1934, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 4070; *Brit. Chem. Abs.* **B**, 1935, 182.

[41] H. S. Young, U. S. P. 2,047,606, July 14, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 6010. British P. 448,457, 1936; *Chem. Abs.*, 1936, **30**, 7126.

[42] G. A. Kramer, U. S. P. 1,967,410, July 24, 1934, to Shell Development Co.; *Brit. Chem. Abs.* **B**, 1935, 531; *Chem. Abs.*, 1934, **28**, 5831.

[43] R. F. LeBaron, U. S. P. 1,966,072, July 10, 1934, to Standard Alcohol Co.; *Brit. Chem. Abs.* **B**, 1935, 395, 442; *Chem. Abs.*, 1934, **28**, 5656.

[44] M. B. Markovich and V. V. Pigulevskii, Russian P. 24,880, 1932; *Chem. Abs.*, 1936, **30**, 1809.

[45] R. M. Isham, U. S. P. 1,929,870, Oct. 10, 1933, part to W. B. Pine; *Chem. Abs.*, 1934, **28**, 173; *Brit. Chem. Abs.* **B**, 1934, 751.

HYDROLYSIS OF ACID LIQUORS AND RECOVERY OF ALCOHOLS

The usual method for recovery of the alcohols from the acid liquors obtained by absorption of olefins in sulphuric acid consists, broadly, in dilution of the liquors with water, followed by distillation.[46] The residual dilute acid is then reconcentrated for further use. However, it being known that the tertiary alcohols are rather easily dehydrated to olefins under the influence of quite dilute (0.02 normal) mineral acids, in consequence, practice has sometimes been to neutralize the acid prior to distillation for recovery of such alcohols. Thus, Moravec and Engs[47] add sufficient basic material (e.g., ammonia) to the acid liquor to bring about separation into two layers. The alcohol phase is withdrawn and distilled. Brooks[48] states, however, that the dehydration may be prevented if the distillation is carried out in a vitreous tower countercurrent to steam. Metal, he finds, tends to catalyze the reaction resulting in decomposition of the alcohol. The operation should be rapid and continuous, and under these conditions, it has been found possible to recover 80 per cent of the *ter*-butyl alcohol present in acid solutions containing as much as 35 or 40 per cent sulphuric acid. Prior to distillation, the diluted acid liquor is hydrolyzed by heating at temperatures from 50°C. up to the boiling point of the alcohol. Shtakelburg[49] also reported that the hydrolysis of *ter*-butyl and *ter*-amyl sulphuric acid esters could be accomplished by distillation countercurrent to steam. Higher alcohol concentrations were obtained by this method than by alkaline hydrolysis.

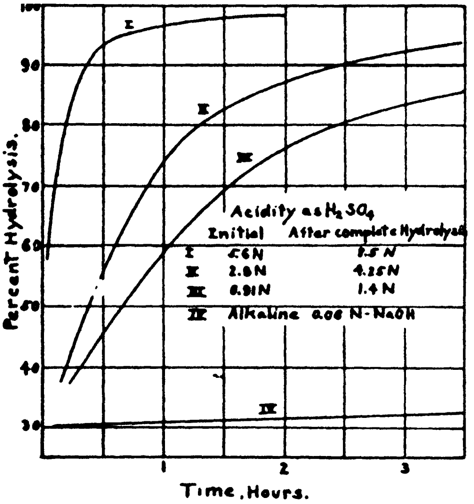

FIG. 106.
Effect of Acid Concentration in the Hydrolysis of *sec*-Monoamyl Sulphate at 100°C. (B. T. Brooks)

Courtesy Industrial and Engineering Chemistry

In the commercial manufacture of the secondary butyl and amyl alcohols, sulphation is generally carried no further than the formation of the monoalkyl sulphate, since this minimizes the development of ethers (which are largely due to dialkyl sulphates). When the dialkyl sulphates are formed, they are precipitated from the acid liquors on dilution with water, and can be withdrawn and hydrolyzed separately. The latter step, in the case of higher monoalkyl sulphates, is catalyzed by sulphuric acid, but requires an appreciable time to proceed to completion even at temperatures up to the boiling point of the alcohol. The hydrolysis time of secondary amyl sulphate under various conditions of temperatures and acid concentration has been studied by Brooks.[50] The results graphically depicted in Fig. 106 represent the effects of varied acid concentration at constant temperature, and strongly indicate the catalytic effect of the hydrogen ion. It will be noticed that in a weakly basic solution, even after three hours, less than 35 per cent hydrolysis had taken place, while in a solution originally 5.6 normal, 93 per cent hydrolysis had occurred in one-half hour. The influence of temperature is shown in Fig. 107. The curves suggest the advisability of using temperatures and acid concentrations as high as possible, while avoiding excessive polymerization. In the case of butyl, amyl and hexyl alcohols, the decomposition of the sulphates to olefins is an important factor in lowering the overall efficiency of the sulphation process. Engs and Moravec[51] suggest that acid liquors, obtained by the solution of secondary olefins in about one equivalent of 90 to 100 per cent sulphuric acid, be diluted to 25 or 35 per cent acid content, and heated.

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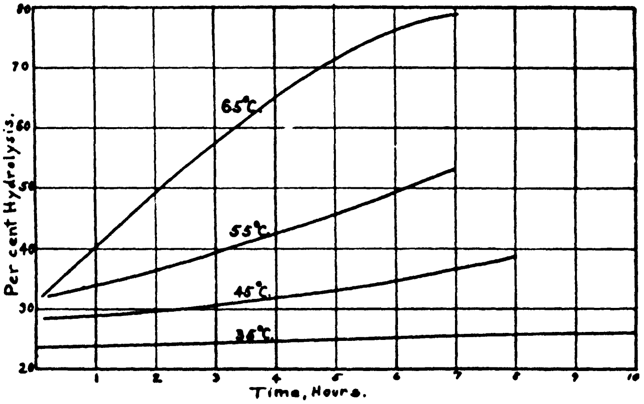
[46] The residual material, consisting of hydrocarbons and unrecovered aliphatic alcohols, may be used as a frothing agent in the recovery of ores by the flotation process. (British P. 441,976, 1936, to American Cyanamid Co.; *Chem. Abs.*, 1936, **30**, 4451; *Brit. Chem. Abs.* **B**, 1936, 603.)

[47] R. Z. Moravec and W. Engs, U. S. P. 2,019,762, Nov. 5, 1935, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 485; *Brit. Chem. Abs.* **B**, 1936, 1192.

[48] B. T. Brooks, *Ind. Eng. Chem.*, 1935, **27**, 278; *Chem. Abs.*, 1935, **29**, 2700; *J. Inst. Pet. Tech.*, 1935, **21**, 226A; *Brit. Chem. Abs.* **B**, 1935, 536.

[49] I. I. Shtakelburg, *Materials on Cracking and Chemical Treatment of Products Obtained, Khimteoret (Leningrad)*, 1935, 188; *Chem. Abs.*, 1935, **29**, 6035.



Courtesy Industrial and Engineering Chemistry

FIG. 107.—Influence of Temperature on the Hydrolysis of *sec*-Monoamyl Sulphate. (B. T. Brooks)

If the mixed secondary and tertiary olefins are absorbed in 90 to 100 per cent sulphuric acid, and allowed to stand, separation takes place. The polymerized tertiary olefins form an oily upper layer, while the secondary alkenes and sulphuric acid compose the lower layer. This latter acid layer is separated, and diluted with water sufficient to give about 15 per cent concentration of acid. The dilute solution is heated to effect hydrolysis, and distilled to recover the alcohols.[52] Engs and Moravec[53] also described a method of producing secondary alcohols in which the diluted liquors are hydrolyzed by heating to a temperature below that at which the alcohol produced distills off. The acid released by this hydrolysis is neutralized before the alcohol is recovered by distillation. In this manner acidity is reduced to a value below that maintained during hydrolysis. Thus, the hydrolytic operation may be carried out at 40° to 100°C. (e.g., 50°C.) in 30 to 40 per cent sulphuric acid solution, and ammonia added to counteract the acid set free.

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[50] B. T. Brooks, *loc. cit.*

[51] W. Engs and R. Z. Moravec, U. S. P. 1,912,695, June 6, 1933, to Shell Development Co.; *Brit. Chem. Abs.* B, 1934, 186; *Chem. Abs.*, 1933, 27, 4240 .

[52] W. Engs and R. Z. Moravec, U. S. P. 1,938,177, Dec. 5, 1933; ***Chem. Abs.***, 1934, **28**, 1048;

In converting dialkyl sulphates into the corresponding alcohols, these investigators[54] treat the compounds with aqueous sulphuric acid (of 60 to 85 per cent strength) to produce first the corresponding monoalkyl sulphates. The latter, in turn, are converted into alcohols by further treatment with water.

When the acid liquors obtained by absorption of secondary olefins in sulphuric acid are diluted, separation ensues, forming two layers. The upper consists largely of hydrocarbons, with some alcohols in solution, while the lower contains the aqueous sulphuric acid solution of the esters. Brooks reports that the secondary alcohols contained in the hydrocarbon layer may be recovered either by washing with aqueous sulphuric acid of 2 to 10 per cent concentration,[55] or by distillation.[56] Simultaneous hydrolysis and separation of the secondary alcohols may be effected, according to Shiffler and Holm,[57] by introducing the diluted olefin-sulphuric acid liquor into the middle section of a reflux still. Alcohol-free sulphuric acid of 70 per cent strength is continuously withdrawn from the foot of the still, while alcohol-rich distillate is obtained at the top. Steam is continuously returned to the lower end of the column to insure complete vaporization of the alcohol.

In the production of butyl, amyl, hexyl and heptyl alcohols, Archibald and Janssen[58] propose to dilute acid reaction liquors with water to an acid concentration between 15 and 50 per cent. The resulting liquid is allowed to stratify, the temperature being kept between 20° and 60°C. as determined by the acid concentration; the higher temperature when settling the more dilute liquors. Under proper conditions, the liquid forms three layers, the top one consisting mainly of polymerized oils, the middle phase containing the major portion of the alcohols, and the bottom layer being dilute acid with only a small proportion of alcohols. The two lower phases may be separately worked up for recovery of the alcohols, e.g., by distillation. Davies[59] proposes, on the other hand, that after separation resulting from the water dilution of the acid liquors, an organic liquid miscible with both layers, such as methanol, ethanol or acetone, be added. The homogeneous mixture which results is hydrolyzed, and the desired alcohols recovered by fractional distillation. Merley[60] treats the alkyl sulphates with such a compound as hexyl acetate, instead of directly hydrolyzing the sulphates to alcohols. The sulphate

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Brit. Chem. Abs. B, 1934, 824; Canadian P. 355,977, 1933; *Chem. Abs.*, 1933, **27**, 5751; both to Shell Development Co.

[53] W. Engs and R. Z. Moravec, U. S. P. 1,938,178, Dec. 5, 1933, *Chem. Abs.*, 1934, **28**, 1048; *Brit. Chem. Abs.* B, 1934, 824. U. S. P. 1,955,416, April 17, 1934; *Chem. Abs.*, 1934, **28**, 3740; *Brit. Chem. Abs.* B, 1935, 182. U. S. P. 1,955,417, April 17, 1934; *Chem. Abs.*, 1934, **28**, 3741; *Brit. Chem. Abs.* B, 1935, 182. All patents to Shell Development Co.

[54] W. Engs and R. Moravec, U. S. P. 1,915,820, June 27, 1933, to Shell Development Co.; *Brit. Chem. Abs.* B, 1934, 136; *Chem. Abs.*, 1933, **27**, 4540.

[55] B. T. Brooks, U. S. P. 1,948,286, Feb. 20, 1934, to Standard Alcohol Co.; *Brit. Chem. Abs.* B, 1934, 1094; *Chem. Abs.*, 1934, **28**, 2723.

[56] B. T. Brooks, U. S. P. 1,944,400, Jan. 23, 1934, to Standard Alcohol Co.; *Brit. Chem. Abs.* B, 1934, 953; *Chem. Abs.*, 1934, **28**, 2013.

[57] W. H. Shiffler and M. M. Holm, Canadian P. 355,672, 1936, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 2577. U. S. P. 2,061,810, Nov. 24, 1936; *Chem. Abs.*, 1937, **31**, 700. French P. 799,076, 1936; *Chem. Abs.*, 1936, **30**, 7582.

[58] F. M. Archibald and P. Janssen, U. S. P. 2,014,078, Sept. 10, 1935, to Standard Alcohol Co.; *Chem. Abs.*, 1935, **29**, 7343; *Brit. Chem. Abs.* B, 1936, 969.

[59] J. A. Davies, U. S. P. 1,966,166, July 10, 1934, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1934, **28**, 5468; *Brit. Chem. Abs.* B, 1935, 395.

[60] S. R. Merley, U. S. P. 1,924,616, Aug. 29, 1933, to Doherty Research Co.; *Chem. Abs.*, 1933, **27**, 5338; *Brit. Chem. Abs.* B, 1934, 534.

and the acetate are mixed by vigorous agitation, without heating, and an anhydrous salt of a monocarboxylic acid (e.g., calcium acetate) is added slowly. The mixture is then heated to complete the reaction, and dry aliphatic alcohol is added to neutralize any excess organic acid evolved. The mixture is refluxed and dry lime is added to neutralize any free sulphuric acid. The resulting alcohols and esters are dry distilled.

Polymerized hydrocarbons may be removed from the hydrolyzed sulphate liquors by repeated extraction with a water-immiscible solvent which is capable of forming azeotropic mixtures with water, (e.g., benzene, carbon tetrachloride, ethylene dichloride, cyclohexane, or propyl acetate). The extract and the raffinate are separated, and the latter is distilled to give an aqueous alcohol distillate. This is then subjected to azeotropic distillation in the presence of the extraction agent to obtain finally water-free and polymer-free alcohol.[61] Carney,[62] on the other hand, reports that dehydration may be effected by rectification of aqueous alcohol in the presence of an agent which does not form azeotropic mixtures. Dehydration is brought about by adding a paraffin hydrocarbon in the vapor phase at atmospheric pressure, and distilling off water vapor and the paraffinic compound under reduced pressure. The added compound is substantially insoluble in water, but miscible with the anhydrous alcohol. Removal of impurities of disagreeable odors (such as polymerized hydrocarbons) from diluted or neutralized sulphuric esters may also be achieved by extraction with the sulphur dioxide (Edeleneau) extract of mineral oil, or similar material of appropriate boiling range.[63] It has also been proposed that the separation of the polymers may be effected by a three step process. In the first stage, the diluted acid liquor is distilled to obtain an azeotropic ternary mixture of alcohol-water-polymer composition. This distillate is dehydrated by employment of solid drying agents such as copper sulphate, calcium oxide or calcium chloride. The dried alcohol-polymer mixture can then be fractionated to yield alcohol substantially free of polymers.[64]

Tertiary alcohols admixed in secondary olefins may be removed by prolonged refluxing with sulphuric acid, or similar mineral acid of low volatility.[65] Concentrated sulphuric acid diluted with not more than its own volume of water is added (in quantity of about 10 to 20 per cent by volume) to the material to be treated. The tertiary alcohols present are dehydrated to olefins, and readily separated. Objectionable sulphur compounds, such as mercaptans, which impart odor or color to the alcohols may be removed from isopropyl and higher secondary alcohols by washing with an aqueous solution of sodium plumbite.[66] Aliphatic alcohols of from 3 to 7 carbon atoms may be freed of organic sulphur and oxygenated compounds imparting objectionable odors by subjection to the action of brass turnings at 350-600°C. Iron sulphide or cobalt oxide may also be employed. The vapors are contacted with the catalyst at the rate of 2 to 5 volumes of alcohol (liquid) to 1 of contact agent per hour.[67] Archibald and Janssen[68] advise refining the olefinic materials from which alkyl sulphates and, subsequently, alcohols are to be made before acid treatment. They suggest passing the hydrocarbon in vapor phase over a refractory catalyst such as bauxite, kaolin or silica gel at a temperature of 225° to 500°C. The treated material is then scrubbed with sodium hydroxide to remove hydrogen sulphide, and subsequently contacted with acid to remove tertiary olefins. The secondary olefins remaining can then be converted to alcohols.

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[61] A. J. van Peski and W. C. B. Smithuysen, U. S. P. 1,954,506, April 10, 1934, to Shell Development Co.; *Brit. Chem. Abs.* **B**, 1935, 182; *Chem. Abs.*, 1934, **28**, 3740. French P. 758,141, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 3079. German P. 616,515, 1935; *Chem. Abs.*, 1936, **30**, 485. British P. 411,303, 1934; *J. Inst. Pet. Tech.*, 1934, **20**, 462A; *Chem. Abs.*, 1934, **28**, 6443. See also W. H. Shiffler and R. C. Mithoff, U. S. P. 2,000,043, May 7, 1935, to Standard Oil of California; *Brit. Chem. Abs.* **B**, 1936, 537; *Chem. Abs.*, 1935, **29**, 4021.

[62] S. C. Carney, Canadian P. 360,257, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 7120.

[63] H. F. J. Lorang and P. W. van der Sluijs, U. S. P. 2,066,400, July 2, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 5457. Dutch P. 31,933, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 3740. German P. 593,441, 1934; *Chem. Abs.*, 1934, **28**, 3079.

[64] S. L. Langedijk, U. S. P. 1,990,789, Feb. 12, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 2174. Dutch P. 34,371, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1935, **29**, 2973. Also S. R. Merley, U. S. P. 1,928,132, Sept. 26, 1933, to Doherty Research Company; *Brit. Chem. Abs.* **B**, 1934, 750; *Chem. Abs.*, 1934, **28**, 493.

[65] H. E. Buc, U. S. P. 1,911,798, May 30, 1933, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1934, 186; *Chem. Abs.*, 1933, **27**, 3943.

[66] F. M. Archibald and C. M. Beamer, U. S. P. 1,995,597, March 26, 1935, to Standard Alcohol Co.; *Brit. Chem. Abs.* **B**, 1936, 310; *Chem. Abs.*, 1935, **29**, 2973.

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[67] R. Rosen and F. M. Archibald, U. S. P. 2,068,872, Jan. 26, 1937, to Standard Oil Development Co.; *Chem. Abs.*, 1937, **31**, 1821.

[68] F. M. Archibald and P. Janssen, U. S. P. 2,035,449, March 31, 1936, to Standard Alcohol Co.; *Chem. Abs.*, 1936, **30**, 3629.

Chapter 17

Properties and Uses of Higher Secondary and Tertiary Alcohols Derived from Olefins

The two types of alcohols produced from olefins of more than 3 carbon atoms are sharply differentiated in both chemical and physical properties. In the discussions of the preceding chapters reference has been made to the readiness with which tertiary alcohols are dehydrated to olefins, the ease with which the latter polymerize, and to the greater stability of the corresponding secondary alcohols. It is evident that this sharp distinction will materially influence the utilization and economic value of the two classes of compounds. It is not surprising then, that heretofore the secondary alcohols have found more extensive commercial application, particularly in the form of their esters, than the tertiary alcohols.

So far as is known, no primary alcohols are formed in the hydration of olefins by the sulphuric acid method, although the remarkable influence of the peroxides on the combination of olefins with the hydrogen halides would indicate the possibility of obtaining primary alcohols by the intermediate formation of the corresponding alkyl chloride or bromide.[1] Since the higher primary alcohols possess certain definite advantages over the corresponding secondary and tertiary alcohols, any commercially feasible method of producing them directly from olefins would be highly attractive. So far, however, no such method has been introduced.

PROPERTIES OF SECONDARY ALCOHOLS

Perhaps the most characteristic reactions of the secondary alcohols are those of dehydration and dehydrogenation. The last-named reaction may be effected either catalytically at temperatures above 200°C. or by oxidation in the vapor phase with a limited amount of oxygen or air, to yield the corresponding ketones. Primary alcohols under like treatment furnish aldehydes, whereas tertiary alcohols do not undergo this simple type of dehydrogenation. The production of ketones from secondary alcohols either by oxidation or catalytic treatment is important industrially and is discussed in Chapter 18. Oxidation of secondary alcohols in chromic acid-aqueous sulphuric acid solution may be rendered quantitative, and serves as a general method of estimating the individual alcohols of this class. By isolation and identification of the ketone produced under these circumstances, the related alcohol can be simultaneously identified and determined.

Dehydration of Secondary Alcohols. Dehydration of these alcohols to the corresponding olefins proceeds, in general, more readily than that of primary and much less easily than with tertiary alcohols. It may be accomplished either in the vapor phase employing contact agents such as alumina, thoria, zirconia or certain acid phosphates of cadmium or manganese, or in the liquid phase in the presence of such strong mineral acids as phosphoric or sulphuric. The exact composition of the olefin mixture formed depends to a large extent on the nature of the catalyst and the operating conditions. Considerable polymerization is frequently encountered, inasmuch as these dehydrating catalysts are usually polymerizing agents as well.[2] Thus, dehydration of the pentanol, 1,2-dimethylpropanol-1, in the presence of 75 per cent sulphuric acid at 80°C., yielded two decenes, 3,5,5-trimethylheptene-2 and 3,4,5,5-tetramethylhexene-2, in about equal quantities.[3]

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[1] See Chapter 33.

On the other hand, Drake and Veitch[4] point out that butanol-2 treated in a similar manner (with 75 per cent sulphuric acid at 80°C.) furnishes no appreciable quantity of octenes. Despite the fact that reaction temperatures were varied from 25° to 100°C. and acid strengths from 50 to 90 per cent, no perceptible yield of the dimer of butene could be obtained. In this case, butene was formed so rapidly, it was believed, that the olefin escaped from the reaction zone before polymerization took place. However, when acid concentration greater than 90 per cent was used, a high-boiling polymer of the type $(C_4H_8)_x$; where x was greater than 2, was secured.

Experiments were undertaken in which the escape of the butene was prevented, and polymerization took place under pressure at 80°C. in about 48 hours, when using acid of 75 per cent strength. Still, however, the yield of octene was low, due to the readiness with which it, in turn, polymerized to still higher olefins. Distillation of this unsaturated hydrocarbon in the presence of a very small quantity of acid resulted in the formation of these higher polymers and also a considerable proportion of di-*sec*-butyl ether in the higher boiling fraction. Ozonolysis of the octene fraction indicated that it was largely 3,4-dimethylhexene-2.[5]

According to Komarewsky, Johnstone and Yoder,[6] there has been some disagreement as to the butenes produced by the dehydration of butyl alcohols. They suggest that a part of the difficulty may have been in the identification of the butenes when the determination was made by bromination of the product. It is proposed that careful fractionation of the butene itself be relied on.

This method of analysis showed that the products of dehydration of *sec*-butyl, alcohol, over a catalyst of phosphoric acid on alumina, were butene-1 and butene-2 in the ratio of 1 to 8. These investigators report that phosphoric acid has a distinct tendency to bring about isomerization of the unsaturated compounds produced, to an extent varying, apparently, with the type of catalyst support used. Thus, when the phosphoric acid on alumina was substituted by phosphoric acid on pumice, the dehydration products were butene-1 and butene-2, but in ratio now of 47.5 per cent to 52.5 per cent.

Dehydration of the higher secondary alcohols often takes an unusual course, with the result that no hypothesis of mechanism hitherto advanced adequately explains the observed results. The usual result of such reaction is a β-alkene, but in several instances considerable quantities of the α-alkene have been reported. Thus, Whitmore and Homeyer[7] report dehydrating the *sec*-heptanol 4,4-dimethylpentanol-2 by distillation from 100 per cent sulphuric acid. Two heptenes were obtained, 4,4-dimethylpentene-1 and 4,4-dimethylpentene-2, in the ratio of 18 to 82. Phosphoric acid, Whitmore and Herndon[8] found, converts octanol-2 (capryl alcohol) into a mixture of octene-1 and octene-2, but in this case the α-octene exceeded the β-octene by 2 to 1. Under pressure and at higher temperatures, extensive rearrangement of the products of a dehydration reaction may take place. Whitmore and Meunier[9] observed that *ter*-butylmethyl carbinol, (3,3-dimethylbutanol-2) at 300°C. and under 2500 pounds pressure furnished only a small yield of 3,3-dimethylbutene-1. The bulk of the product was a mixture of the rearranged olefins 2,3-dimethylbutene-2 and 2,3-dimethylbutene-1 in the ratio of 2 to 1.

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[2] See Chapter 26 for material on polymerization of olefins, and polymerization catalysts.

[3] N. L. Drake, G. M. Kline and W. G. Rose, *J.A.C.S.*, 1934, **56**, 2076; *Chem. Abs.*, 1935, **29**, 113; *J. Inst. Pet. Tech.*, 1934, **20**, 609A; *Brit. Chem. Abs.* **A**, 1934, 1329.

[4] N. L. Drake and F. P. Veitch, *J.A.C.S.*, 1935, **57**, 2623; *J. Inst. Pet. Tech.*, 1936, **22**, 88A; *Brit. Chem. Abs.* **A**, 1936, 311; *Chem. Abs.*, 1936, **30**, 1735.

[5] See Chapter 39 for a discussion of this type of identification.

[6] V. Komarewsky, W. Johnstone and P. Yoder, *J.A.C.S.*, 1934, **56**, 2705; *Chem. Abs.*, 1935, **29**, 724; *Brit. Chem. Abs.* **A**, 1935, 192.

[7] F. C. Whitmore and A. H. Homeyer, *J.A.C.S.*, 1933, **55**, 4194; *Chem. Abs.*, 1933, **27**, 5716; *Brit. Chem. Abs.* **A**, 1933, 1271.

[8] F. C. Whitmore and J. M. Herndon, *J.A.C.S.*, 1933, **55**, 3428; *Brit. Chem. Abs.* **A**, 1933, 1033; *Chem. Abs.*, 1933, **27**, 4771.

More extensive rearrangement takes place in the case of di-*ter*-butylcarbinol (2,2,4,4-tetramethylpentanol-3) when employing 1-chloro-4-naphthalenesulphonic acid as a dehydrating catalyst. This, probably, is not unusual since neither of the carbon atoms (in this alcohol) next to the carbinol group possesses an attached hydrogen atom. Whitmore and Stahly[10] report that when the reactants were heated in a flask immersed in an oil bath at 180°C., there was no evolution of gas until practically the theoretical quantity of water had escaped. At this point, the distillation temperature dropped sharply from 88° to 34°C., trimethylethylene distilled over, and gas was evolved. After one and one-half hours, the distillation temperature rose, and higher olefins appeared. It was found that a 77 per cent yield of trimethylethylene had been obtained, together with smaller quantities of mixed nonenes, diamylenes and triisobutylenes, while the gas which had been evolved proved to be isobutene. However, when the dehydration was conducted below 155°C., and the water formed was allowed to reflux, splitting of the hydrocarbon molecule did not occur. In this instance nonenes to the extent of 71 per cent were formed. When the latter, admixed with the chloronaphthalenesulphonic acid, were heated to 145-205°C., then decomposition did occur. The hydrocarbon products thus obtained consisted of 68 per cent trimethylethylene, 50 per cent isobutene and 39 per cent polymers.

Condensation With Aromatics. Secondary alcohols condense with aromatic hydrocarbons in the presence of sulphuric acid, to yield the corresponding secondary alkyl derivative. Kirrmann and Graves[11] prepared isopropylbenzene and polyisopropylbenzenes by this type of reaction, using benzene and isopropyl alcohol in the presence of concentrated sulphuric acid. Toluene and isopropyl alcohol yield both the ortho and para derivatives of cymene, when the condensing agent is 80 per cent sulphuric acid.[12] According to Durand,[13] the original discovery of the interaction of alcohols with benzene hydrocarbons was made by Liebmann,[14] and subsequently extended by Goldschmidt,[15] Brochet and LeBoulenger,[16] and Verley.[17]

Tzukervanik[18] points out that combination of benzene with secondary or tertiary alcohols can be effected most readily in the presence of aluminum chloride. This investigator believes that reaction probably involves the intermediate formation of alcohol-aluminum chloride complexes of the type $AlCl_2(OR)$ (with elimination of hydrogen chloride) as these have been shown to result on treatment of primary

[9] F. C. Whitmore and P. L. Meunier, *J.A.C.S.*, 1933, 55, 3721; *Chem. Abs.*, 1933, 27, 5053; *Brit. Chem. Abs.* A, 1933, 1140.

[10] F. C. Whitmore and E. E. Stahly, *J.A.C.S.*, 1933, 55, 4153; *Chem. Abs.*, 1933, 27, 5715; *Brit. Chem. Abs.* A, 1933, 1271.

[11] A. Kirrmann and M. Graves, *Bull. soc. chim.*, 1934, (5) 1, 1494; *Brit. Chem. Abs.* A, 1935, 203; *Chem. Abs.*, 1935, 29, 2516.

[12] H. Meyer and K. Bernhauer, *Monatsh.*, 1929, 53 and 54, 721; *Chem. Abs.*, 1930, 24, 346; *Brit. Chem. Abs.* A, 1929, 1441. See also G. Desseigne, *Compt. rend.*, 1935, 200, 466; *Chem. Abs.*, 1935, 29, 2927; *Brit. Chem. Abs.* A, 1935, 612.

[13] J. F. Durand, *Bull. soc. chim.*, 1935, (5) 2, 824; *Chem. Abs.*, 1935, 29, 5820; *Brit. Chem. Abs.* A, 1935, 852.

[14] A. Liebmann, *Ber.*, 1881, 14, 1842; *Chem. Zentr.*, 1881, 3, 685.

[15] H. Goldschmidt, *Ber.*, 1882, 15, 1066, and 1425; *Chem. Zentr.* 1882, 3, 636.

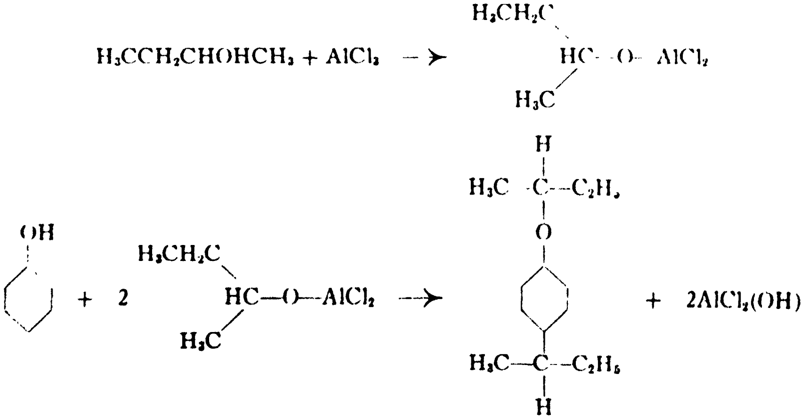
[16] A. Brochet and P. LeBoulenger, *Compt. rend.*, 1893, 117, 235; *Chem. Zentr.*, 1893, 2, 429.

[17] A. Verley, *Bull. soc. chim.*, 1898, 19, (3) 67; *Chem. Zentr.*, 1898, 1, 450.

[18] I. Tzukervanik, *J. Gen. Chem. (U.S.S.R.)*, 1935, 5, 117; *Chem. Abs.*, 1935, 29, 4746; *Brit. Chem. Abs.* A, 1935, 967.

alcohols with the metallic halide. Tzukervanik and Tokareva[19] observed that isopropyl and *sec*-butyl alcohols reacted with benzene and toluene (in the presence of the Friedel-Crafts reagent) to yield up to 70 per cent of alkylated hydrocarbons. If an excess of aluminum chloride is used, some dialkyl derivatives are secured. With toluene, the alkyl group is directed to the para position. Thus, 30 g. of isopropyl alcohol; 150 cc. of benzene and 43 g. of aluminum chloride gave 35 g. of a liquid fraction consisting of cumene and diisopropylbenzene. The same quantities of isopropyl alcohol and aluminum chloride reacted with 100 cc. of toluene yielded 35 g. of *p*-cymene. Secondary butyl alcohol (20 grams), benzene (100 cc.) and aluminum chloride (30 grams) furnished *sec*-butylbenzene.

Condensation With Phenols. Huston and Hsieh[20] have investigated the reactions of secondary, tertiary and primary alcohols with phenol and benzene derivatives in the presence of aluminum chloride. They report that, as a general rule, tertiary alcohols condense readily with phenols to give good yields of *p-ter*-alkylphenols (45 to 60 per cent). Under the same conditions, isopropanol gave a small yield of a substance which was not identified, but did not correspond in properties to any known propyl phenol or phenyl propyl ether. Neither *sec*-butyl alcohol nor primary alcohols reacted with benzene. Tertiary alcohols did so readily, and gave good yields (65 to 70 per cent) of products. Secondary alcohols reacted more slowly, and resulted in lower yields of alkylbenzenes, and the primary alcohols did not condense under the conditions obtaining. Tzukervanik and Nazarova[21] observed that tertiary alcohols and phenol furnished yields of 60 to 70 per cent of alkylated phenols (together with alkylated benzene hydrocarbons as by-products). Furthermore, these investigators are of the opinion that the use of secondary alcohols gives rise mainly to ethers of alkylated phenols. Thus, they report obtaining isopropylcumyl ether ($C_3H_7—C_6H_4OC_3H_7$) from isopropanol and phenol. This difference in the reactions of secondary and tertiary alcohols (under the influence of aluminum chloride) is attributed to the fact that secondary alcohols do not readily yield considerable amounts of olefins and alkyl halides, whereas the tertiary alcohols do. Condensation of secondary alcohols is believed to take place according to the following scheme:



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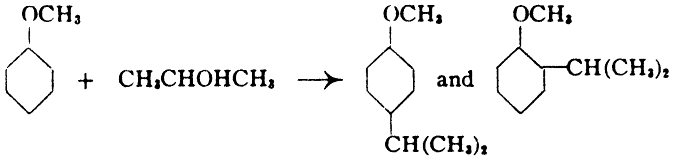
[19] I. Tzukervanik and K. Tokareva, *J. Gen. Chem. (U.S.S.R.)*, 1935, 5, 764; *Brit. Chem. Abs.* A, 1936, 61; *Chem. Abs.*, 1936, 30, 442.

[20] R. C. Huston and T. Y. Hsieh, *J.A.C.S.*, 1936, 58, 439; *Chem. Abs.*, 1936, 30, 2939; *Brit. Chem. Abs.* A, 1936, 602; *J. Inst. Pet. Tech*, 1936, 22, 254A.

[21] I. Tzukervanik and Z. Nazarova, *J. Gen. Chem. (U.S.S.R.)*, 1935, 5, 767; *Chem. Abs.*, 1936, 30, 443.

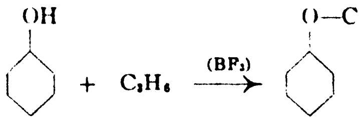
In confirmation of this proposed mechanism, it is pointed out that isopropyl alcohol and anisole (phenylmethyl ether) in the presence of aluminum chloride furnish a mixture of *o*-and *p*-isopropylanisole:



Smith[22] reports that considerable rearrangement of alkyl phenyl ethers may take place in the presence of aluminum chloride. Thus, *sec*-butylphenyl ether is transformed into *p*-*sec*-butylphenol. This investigator states the corresponding *ter*-butylphenyl ether rearranges so readily that it cannot be distilled at atmospheric pressure without thermal isomerization to *p*-*ter*-butylphenol taking place. Such change occurs even more rapidly with the condensation product of isobutyl alcohol and phenol, it is said, so that there is some doubt that isobutyl phenyl ether can be prepared, the substance actually obtained being the isomer, *ter*-butylphenol.

That boron trifluoride exerts catalytic action in bringing about the interaction of secondary alcohols and phenols has been demonstrated by Sowa, Hennion and Nieuwland.[23] They reacted 60 grams of isopropyl alcohol with 94 grams of phenol in the presence of 24 grams of the trifluoride. A mixture of alkylated phenols and phenol ethers was secured, 47.5 per cent of which was 2-isopropylphenol, 34 per cent 4-isopropylphenol and 18.5 per cent of 2,4-diisopropylphenylisopropyl ether. Since investigation showed that isopropylphenyl ether did undergo rearrangement,[24] as exhibited by butylphenyl ethers, it was believed that this alkylation of phenol in the presence of boron trifluoride involved a primary dehydration of the alcohol to the olefin and the subsequent condensation of the unsaturated hydrocarbon with phenol:

$$C_3H_7OH \longrightarrow C_3H_6 + H_2O$$



Langwell[25] reports that zinc chloride in 80 per cent aqueous solution will serve as the condensation catalyst in this reaction. When secondary alcohols are employed a temperature of about 130°C. is required, as for example, the interaction of phenol and *sec*-isohexanol. In the case of primary alcohols, a temperature of 180°C. is necessary. A volatile hydrocarbon such as isohexene or benzene may be added, and reaction carried out under reflux. Bertonasco[26] reports that warming resorcinol with *sec*-butanol and concentrated sulphuric acid produces a dye. The products are, it is suggested, esters of resorcinol-disulphonic acid.

Physical Properties. The boiling points and densities characteristic of the more important secondary alcohols of the lower range are given in Table 96.

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[22] R. A. Smith, *J.A.C.S.*, 1933, **55**, 3718; *Chem. Abs.*, 1933, **27**, 5067; *Brit. Chem. Abs.* **A**, 1933, 1156.

[23] F. J. Sowa, G. F. Hennion and J. A. Nieuwland, *J.A.C.S.*, 1935, **57**, 709; *Chem. Abs.*, 1935, **29**, 3321; *Brit. Chem. Abs.* **A**, 1935, 744.

[24] R. A. Smith, *loc. cit.*

[25] H. Langwell, British P. 424,506, 1935, to British Industrial Solvents Ltd.; *Chem. Abs.*, 1935, **29**, 4376; *Brit. Chem. Abs.* **B**, 1935, 443. French P. 778,890, 1935; *Chem. Abs.*, 1935, **29**, 4855.

[26] E. Bertonasco, *G. Farm. Chim. Sci. affini*, 1935, **84**, 58; *Brit. Chem. Abs.* **A**, 1936, 1104; *Chem. Zentr.*, 1935, **2**, 3096.

Relatively few of these have been definitely identified among the complex mixture obtained by the sulphation of the higher olefins. The most important secondary alcohols being produced from the lower olefins aside from isopropanol are, perhaps, butanol-2, pentanol-2 and pentanol-3, and secondary hexyl and heptyl alcohols of undetermined structure.

The water solubilities of secondary alcohols above isopropyl alcohol decrease rapidly. Although the latter is miscible in all proportions with water, butanol-2 and pentanol-2 dissolve to a limited extent in water, and pentanol-3, hexanol-2 and hexanol-3 are very slightly soluble. The secondary heptanols and octanols are practically insoluble, as are the higher members of the series. Although butanol-2 is somewhat soluble in pure water, it may readily be salted out of solution by addition of calcium chloride. Thus, Shaposhnikov and Pinchuk[27] find that butyl and higher alcohols may be determined quantitatively by this method. They suggest adding 4 cc. of the solution to be tested to 20 cc. of aqueous calcium chloride (of density 1.16) which has been saturated previously with butyl alcohol. The higher alcohols are sufficiently insoluble so that the solution of the chloride need not be saturated with them, presumably. Separation occurs under this treatment, and the alcohol layer formed contains the butyl and higher alcohols present together with any hydrocarbons. The latter are determined by adding 35 volumes of water, to the alcohol layer, and noting volume of hydrocarbons formed. This quantity is subtracted from that previously ascertained as representing alcohols and other liquids.

TABLE 96.—*Some Higher Secondary Aliphatic Alcohols.*[28]

Alcohol	Boiling Point °C.	Melting Point °C.	Density 20°/4°C.	Molecular Weight
Butanol-2	99.5		0.808	74.08
Pentanol-2	119.5		0.809	88.09
Pentanol-3	115.6		0.815	88.09
3-Methylbutanol-2	114		0.819	88.09
Hexanol-2	131.9		0.803	102.11
Hexanol-3	135		0.819	102.11
3,3-Dimethylbutanol-2	121-123	5.5	0.812	102.11
2-Methylpentanol-3	128		0.824	102.11
3-Methylpentanol-2	134		0.831	102.11
4-Methylpentanol-2	130-132		0.828	102.11
Cyclohexanol	161.5	23.9	0.962	100.09
Heptanol-2	158		0.819	116.12
Heptanol-3	66(18mm.)		0.823	116.12
Heptanol-4	155.4		0.820	116.12
2-Methylhexanol-3	141		0.821(17°)	116.12
2-Methylhexanol-4	148.2		. . .	116.12
2-Methylhexanol-5	150		0.819(17°)	116.12
3-Methylhexanol-4	150		0.852	116.12
2,4-Dimethylpentanol-3	140		0.829	116.12
Cycloheptanol	185.2		0.958	114.11
2-Methylcyclohexanol-1	169		0.923	114.11
3-Methylcyclohexanol-1	176	−47	0.914	114.11
4-Methylcyclohexanol-1	174		0.924(14°)	114.11

ESTERS OF THE HIGHER SECONDARY ALCOHOLS

The esters of the secondary alcohols, particularly the acetates, are important as solvents in the lacquer and varnish industry. Parks and Hopkins[29] report that the secondary acetates are miscible in all proportions with the other solvents and diluents commonly used in the production of lacquers, and may be employed in any desired proportion. Asphalt, tars, pitches, rosin, ester gum and many other resins are soluble in these liquids, although shellac is not. The physical characteristics of mixtures of 85 per cent secondary acetates with about 15 per cent of the corresponding alcohols are summarized in Table 97.

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[27] V. G. Shaposhnikov and S. E. Pinchuk, *Trudui. Gosudarst. Opuit. Zavoda Sintet. Kauchuka Litera B. III. Synthetic Rubber*, 1934, 104; *Chem. Abs.*, 1936, 30, 4787.

[28] Data from International Critical Tables. McGraw-Hill Book Co., Inc., New York, 1926.

[29] J. G. Parks and M. B. Hopkins, *Ind. Eng. Chem.*, 1930, 22, 826; *Chem. Abs.*, 1930, 24, 4646;

TABLE 97.—*Properties of Secondary Acetates (With 15 Per Cent of Alcohol)*

Ester	Boiling Point °C.	Density 15.5/18.5°C.	$N^{20°C.}$
sec-Butylacetate	107-114	0.861	1.3915
sec-Amylacetate...	128-134	0.863	1.4021
sec-Hexylacetate....	146-156	0.863	1.4081

The solvent power of these esters, as evidenced by dilution ratios and viscosity measurements of cellulose nitrate solutions, is only slightly less than that of the corresponding primary esters, it was reported. Parks and Hopkins also point out that the solubility of water in the solvent is an indication of the probable tendency of that medium to cause blushing in humid weather. As a general rule the aliphatic esters boiling above 100°C. are only very slightly miscible with water, and therefore have good blush resistance. Very little difference was observed in this respect between normal and secondary esters. Sayers, Schrenk and Patty[30] made a study of the physiological properties of commercial butyl acetate. The characteristic action of pure *n*-butyl acetate appears to be strongly narcotic, with the expected consequence of coma and death if the vapors are breathed in high concentration. Animals which were exposed to the fumes and narcoticised recovered completely if death did not take place during the period of exposure. Commercial butyl acetate produces symptoms of nasal and eye irritation, and narcosis. At room temperature, however, it was not possible to attain a concentration of vapor that was dangerous to the life of guinea pigs in 30 to 60 minutes. Exposure to 1 to 1.4 per cent vapor concentration is dangerous, however, after several hours. Concentrations greater than 0.7 per cent cannot be endured without effects more serious than the eye and nose irritation within one hour. If exposure is continued for several hours, 0.33 per cent is the maximum that can be tolerated with but slight, or no symptoms. The commercial material used in the investigation had a marked odor, and was found to be distinctly irritating (to the nose and eyes of men) in concentrations apparently harmless to guinea pigs after a single exposure of several hours' duration. The lower inflammability limit was estimated to be approximately 1.7 per cent, but concentrations well below this figure are extremely disagreeable to men from the standpoint of odor and eye and nose irritation, it was reported.

Bass and Fenn[31] describe the preparation of *sec*-butyl lactate (boiling at 172°C., density 0.972) by heating butanol-2 and anhydrous lactic acid at 170° to 175°C. for four hours in a pressure vessel. An acid catalyst may be used to promote esterification. The product is then separated by fractionation. Cyclohexanol may be reacted with acetic acid, according to Zal'kind and Gerchikov,[32] by mild heating with 10 per cent excess of acetic acid and 0.3 per cent sulphuric acid for one-half hour. A yield of 83 per cent was obtained. Under the same conditions the sec-

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Brit. Chem. Abs. B, 1930, 1038. See also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[30] R. R. Sayers, H. H. Schrenk and F. A. Patty, *U. S. Pub. Health Repts.*, 1936, 51, 1229; *Chem. Abs.*, 1936, 30, 7690.

[31] S. L. Bass and H. N. Fenn, U. S. P. 1,956 972, May 1, 1934, to Commercial Solvents Corp.; *Chem. Abs.*, 1934, 28, 4072; *Brit. Chem. Abs.* B, 1935, 262.

[32] Y. S. Zal'kind and M. G. Gerchikov, *Plastischeskie Massui*, 1934, No. 3, 37; *Chem. Abs.*, 1934, 28, 6708.

ondary heptyl alcohol, methylcyclohexanol, gives 78 to 80 per cent of the corresponding ester. Acetic acid as dilute as 60 per cent was said to be satisfactory in making this preparation. Cyclohexanol and 85 per cent formic acid, when allowed to stand in the cold without catalyst for 24 hours, gave 85 to 90 per cent of the formate. The monoester of oxalic acid could not be prepared, although by refluxing cyclohexanol with the anhydrous acid, the dicyclohexyl oxalate was obtained.

ETHERS OF HIGHER SECONDARY ALCOHOLS

The method of making an ether from the corresponding alcohol, by dehydration in the presence of sulphuric acid, may be applied to the higher aliphatic ethers. Thus, Hennion, Hinton and Nieuwland[33] prepared ethers by heating the corresponding alcohols with sulphuric acid while removing water in the vapor form. Reaction was carried out until the temperature of the mixture reached a point midway between the boiling point of the alcohol and that of the ether. The latter was isolated by cooling the mixture, diluting with water, then washing with aqueous sodium hydroxide, and distilling. Other acids, such as phosphoric or benzenesulphonic, have been proposed as the dehydrating agent. To facilitate continuous removal of water during reaction, a water-immiscible entraining agent which forms an azeotrope with water having a minimum boiling point (e.g., a light gasoline fraction) may be added to the reaction mixture. In the case of *n*-butyl alcohol, however, it is said that the products form a mixture of minimum boiling point with water, making unnecessary addition of an entraining agent.[34]

As an alternative procedure, sulphuric acid solutions of olefin may be used. A continuous process has been described,[35] in which such acid liquors are hydrolyzed with water and distilled. That portion of the distillate consisting of alcohol and water is returned to the hot acid liquor for further dehydration.

It has been reported,[36] however, that the higher ethers (those from alcohols having more than 7 carbon atoms per molecule) may be produced in alkaline media. The starting materials in this instance are sulphuric or phosphoric acid esters of the alcohol, which are heated with the alcohol or a phenol, in alkaline media, or with alcoholates or phenolates.

INDUSTRIAL APPLICATIONS OF SECONDARY BUTYL ALCOHOL

Ellis[37] finds that *sec*-butyl alcohol may be used as an homogenizer in the preparation of a nitrocellulose coating composition. A low viscosity nitrocellulose is dissolved in 40 parts of diacetone alcohol, 30 parts of a cracked petroleum distillate (boiling between 70° and 120°C.) as a diluent and viscosity reducer, and 30 parts of *sec*-butyl alcohol. A compatible synthetic resin may be incorporated, or if a colored lacquer is to be produced, a pigment may be ground in with the solvents. Such liquid compositions may be applied over varnish coatings without dissolving and disintegrating the undercoat.

As has been stated, the characteristic oxidation reaction of the secondary alcohols leads to the production of ketones.[38] However, certain methods of oxidation

[33] G. F. Hennion, H. D. Hinton and J. A. Nieuwland, *Proc. Indiana Acad. Sci.*, 1933, 42, 109; *Chem. Abs.*, 1933, 27, 5716; *Brit. Chem. Abs.* A, 1934, 277.

[34] British P. 243,736, 1926, to Distilleries des Deux-Sevres; *Brit. Chem. Abs.* B, 1926, 768.

[35] British P. 362,593, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1932, 332.

[36] British P. 401,142, 1933, to Henkel & Co., G. m. b. H.; *Brit. Chem. Abs.* B, 1934, 54; *Chem. Abs.*, 1934, 28, 2365. French P. 751,923, 1933; *Chem. Abs.*, 1934, 28, 777.

[37] Carleton Ellis, U. S. P. 1,984,061, Dec. 11, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1935, 29, 948; *Brit. Chem. Abs.* B, 1935, 1152.

[38] Such reactions are discussed in Chapter 18.

give rise to acids containing fewer carbon atoms. Thus, Pelton and Kennedy[39] suggest that *sec*-butyl alcohol be reacted with a fused mixture of potassium and sodium hydroxides at 200°-325°C. to give propionic acid. Strosacker, Kennedy and Pelton[39a] report that *sec*-butyl alcohol and propyl alcohol may be mixed and subjected to the action of fused caustic soda to obtain alkali propionates.

Hardy[40] has reported another type of reaction producing acids or their esters. *sec*-Butyl alcohol was condensed at 200°C. to 210°C. with carbon monoxide in the presence of phosphoric acid containing a small amount of copper phosphate. From one kilogram of the alcohol, about 29 grams of the methyl ester of pivalic (trimethylacetic) acid and 10.5 grams of the methyl ester of methylethylacetic acid resulted.

Among the uses for which the secondary alcohols have been suggested is included the production of esters. Much work has been done in consequence, with a view to facilitating and improving the processes used in extracting water from the alcohols, and for increasing the purity of the product. In procedures designed to render the alcohol anhydrous, some care must be taken that it is not dehydrated to the olefin, though the secondary alcohols, as compared with the tertiary, are fairly stable in this respect. As pointed out before, the higher alcohols are only slightly soluble in water, nor are large proportions of water soluble in the alcohols. Those of the octyl and nonyl range are not ordinarily contaminated by large quantities of water, but neither have they so far become of industrial importance. The greatest interest has centered on the secondary butyl and amyl alcohols. The majority of methods proposed for rendering these anhydrous depend on the use of entraining agents or solvent extraction, and frequently both. Taylor[41] suggested that carbon tetrachloride be used as an agent for drying the higher alcohols. The alcohols may first be extracted with carbon tetrachloride, whereby a large proportion of the water present is eliminated. That taken up in the extract can then be removed by distillation as a ternary azeotrope with carbon tetrachloride and alcohol. Finally, methyl alcohol is added, and the carbon tetrachloride and methanol removed as a binary azeotrope. If the secondary alcohol does not form a low boiling azeotrope with carbon tetrachloride, or a ternary azeotrope with the tetrachloride and water, the latter is removed in a water-carbon tetrachloride mixture which boils out at 66°C. Shiffler and Mithoff[42] have used a light petroleum ether in an analogous manner. In this case the liquid to be dried (such as *sec*-butyl alcohol) is passed into a stratifying zone, where it is brought in contact with the condensate obtained from a latter stage of the process. This condensate consists of portions of the *sec*-butyl alcohol, water, and petroleum ether. The petroleum ether brings about a separation, acting as solvent for the alcohol, and two layers are formed, one relatively rich in the butanol, and poor in water, while most of the water and a small amount of alcohol form the lower layer. The petroleum layer is passed to a reflux condenser. The vapors from this column are condensed and used in the first step of the process, recirculating through the system in this way.

Lebo,[43] on the other hand, proposes distilling the water and alcohol to a constant-boiling mixture without addition of entraining agents, eliminating the solvent extraction step. Thus, *sec*-butyl alcohol may be distilled to the constant-boiling point, and this distillate collected. A second distillation is then carried out, after adding an entraining agent such as benzene or xylene.

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[39] E. L. Pelton and C. C. Kennedy, U. S. P. 1,926,059, Sept. 12, 1933, to Dow Chemical Co.; *Brit. Chem. Abs.* B, 1934, 709; *Chem. Abs.*, 1933, **27**, 5751.

[39a] C. J. Strosacker, C. C. Kennedy and E. L. Pelton, U. S. P. 1,926,068, Sept. 12, 1933, to Dow Chemical Co.; *Chem. Abs.*, 1933, **27**, 5751.

[40] D. V. N. Hardy, *J.C.S.*, **1936**, 358. *Chem. Abs.*, 1936, **30**, 3776.

[41] R. Taylor, *J.S.C.I.*, 1934, **53**, 193T; *Chem. Abs.*, 1934, **28**, 5400; *Brit. Chem. Abs.* B, 1934, 750.

[42] W. H. Shiffler and R. C. Mithoff, U. S. P. 2,000,043, May 7, 1935; *Chem. Abs.*, 1935, **29**, 4021.

[43] R. B. Lebo, U. S. P. 1,911,829, May 30, 1933, to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1934, 393; *Chem. Abs.*, 1933, **27**, 3943.

For the removal of aldehyde impurities that may be present in primary alcohols, Burke[44] suggests a treatment involving refluxing with an amine so chosen that the boiling point of the alcohol being treated is more than 15°C. removed from the boiling point of the amine. The alcohol is distilled in a column into which an amine is admitted at a point near the top (but not at the top, lest the product be contaminated) so that it flows down counter to the ascending vapors. Such amines as aniline, phenylacetyl amine or naphthylamine may be used. Other contaminants, such as mercaptans which impart color and objectionable odor, may be removed by using an aqueous sodium plumbite washing solution.[45]

INDUSTRIAL APPLICATIONS OF THE ESTERS OF SECONDARY BUTANOL

The most important ester of secondary butyl alcohol is the acetate, which is made on a considerable scale.[46] One method suggested for this synthesis[47] proposes that the alcohol and the organic acid be heated together in the presence of a catalyst until equilibrium is reached. The mixture is fractionally distilled, and the condensate allowed to stratify. The water and *sec*-butyl acetate produced are removed in equivalent proportions, and the remainder returned to the column as reflux. Further alcohol and acid are added to compensate for the product extracted. Merley[48] states that the product of esterification may be freed from impurities, such as mercaptans and hydrocarbons, by a system of successive distillations. First, a fractional distillation of the material is carried out, eliminating the major portion of the impurities present. The rectified portion is then redistilled with the addition of water. The product of this last step is finally redistilled to eliminate water. Merley[49] has also pointed out that the small amounts of tertiary esters which may be present (e.g., *ter*-butyl acetate) may be removed by heating with an aqueous solution of a mineral acid (such as sulphuric acid) containing the acid of the ester (in this case, acetic acid). The tertiary ester is decomposed completely, and the more stable secondary ester may be recovered by fractional distillation.

The secondary acetate is finding widespread use as a lacquer solvent and thinner. Blech[50] has suggested the use of *n*-butyl acetate in a hand-cleaner capable of removing lacquer, varnish, printer's ink and similar materials. The composition consists essentially of a soap, water, diatomaceous earth, glycerine and a perfumed detergent and scouring compound, to which a rapid-acting volatile solvent such as *n*-butyl acetate is added to dissolve rapidly the lacquer material present. Wilson[51] proposes that *sec*-butyl acetate be used in the dewaxing of oil. The latter is mixed with the ester, is agitated with a solvent, the solution subsequently cooled and the precipitated wax removed by filtration.

Butyl formate has been found to be definitely toxic, and may be used as an insecticide. Bass and Fenn[52] report that *sec*-butyl lactate may be produced by reacting the anhydrous acid and the secondary alcohol in a reaction bomb. The temperature is raised to 170-175°C., and the reactants maintained at this temperature under pressure for 4 hours. The resultant ester is purified by fractional distillation.

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[44] J. P. Burke, U. S. P. 1.987.601, Jan. 15, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1935, 1129; *Chem. Abs.*, 1935, 29, 1431.

[45] F. M. Archibald and C. M. Beamer, U. S. P. 1.995.597, March 26, 1935, to Standard Alcohol Co.; *Brit. Chem. Abs.* B, 1936, 310; *Chem. Abs.*, 1935, 29, 2973.

[46] See Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, 1934.

[47] K. R. Edlund, U. S. P. 1,952,125, March 27, 1934, to Shell Development Co.; *Brit. Chem. Abs.* B, 1935, 139; *Chem. Abs.*, 1934, 28, 3416.

[48] S. R. Merley, U. S. P. 1,928,132, Sept. 26, 1933, to Doherty Research Co.; *Chem. Abs.*, 1933, 27, 5753; *Brit. Chem. Abs.* B, 1934, 750.

[49] S. R. Merley, U. S. P. 1,898,737, Feb. 21, 1933, to Doherty Research Co.; *Chem. Abs.*, 1933, 27, 2692; *Brit. Chem. Abs.* B, 1933, 955.

[50] W. Blech, U. S. P. 2,064,725, Dec. 15, 1936, to T. B. Gregory; *Chem. Abs.*, 1937, 31, 786.

[51] A. M. Wilson, U. S. P. 2,049,036, July 28, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, 30, 6550.

HIGHER SECONDARY ALCOHOLS

The higher secondary alcohols may be produced by the sulphation process, but those originating from olefins above the heptene range are prepared in lesser quantities in this manner. The most important of the alcohols above *sec*-butanol are *sec*-amyl and *sec*-hexyl, which are made commercially in considerable volume. They have been suggested as solvents in the ozocerite refining process proposed by Cox.[53] The crude ozocerite is agitated with a liquid consisting of 80 per cent *n*-butanol and 20 per cent *sec*-amyl alcohol. The waxy constituents are taken into solution by this alcoholic mixture, while the asphaltic fractions remain suspended in the liquid medium. The process is carried out at a temperature above the melting point of the wax, until the wax solution and the asphaltic particles are thoroughly emulsified. Rapid cooling then causes the waxy constituents to precipitate from solution, carrying the asphaltic material down with them. Heating the mixture subsequently without agitation, redissolves the wax, which can then be separated from the insoluble asphaltic residue. It has also been suggested[54] that the high molecular weight alcohols obtained from olefins are capable of stabilizing a suspension of metal soaps in mineral oils. Relatively small proportions of these heavier alcohols are reported to be sufficient.

The esters of *sec*-hexyl, -heptyl and -octyl alcohols and dicarboxylic acids (such as dioctyl phthalate) may be used as plasticizers with cellulose nitrate, Van Schaack[55] reports. Mixed esters involving lower alcohols as well as these higher secondary compounds may be used.

A number of alkylated benzene homologs and derivatives have been made from the higher secondary alcohols.[56] Austin[57] states that alkyl resorcinols may be prepared by condensing a secondary alcohol (such as heptanol-2) with resorcinol in the presence of a condensing agent. Schrauth[58] reports that interaction of *sec*-amyl alcohol with naphthalene can be carried out in the presence of sulphuric acid to produce a wetting and cleansing agent. Naphthalene sulphonic acid may be used in place of the hydrocarbon. Thus, 600 parts of naphthalene may be converted into naphthalene sulphonic acid by treatment with 720 parts of sulphuric acid at 110° to 180°C. The reaction mixture is cooled to 105°C. and maintained at this temperature while a solution of 620 parts of *sec*-amyl alcohol and 40 parts of sulphuric acid is added over a period of four hours. The mixture is then heated to 125°C. for four more hours. The mass separates into two layers, the lower of which, consisting of sulphuric acid, is withdrawn. From the upper layer, the unaltered sulphuric acid is removed by treatment with lime. The solution of amylated naphthalene sulphonic acid so obtained is neutralized with sodium carbonate to form the sodium salt. The latter is said to be a wetting emulsifying or lathering agent. *sec*-Amyl alcohol may be substituted by cyclohexanol or methylcyclohexanol.

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[52] S. L. Bass and H. N. Fenn, U. S. P. 1,956,972, June 1, 1934, to Commercial Solvents Corp.; *Brit. Chem. Abs.* B, 1935, 262; *Chem. Abs.*, 1934, **28**, 4072.

[53] D. C. Cox, U. S. P. 1,951,861, March 20, 1934, to A. G. Dickinson; *Chem. Abs.*, 1934, **28**, 3579.

[54] French P. 799,072, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 7838.

[55] R. H. Van Schaack, U. S. P. 1,949,093, Feb. 27, 1934, to Van Schaack Bros. Chem. Works, Inc.; *Brit. Chem. Abs.* B, 1935, 13; *Chem. Abs.*, 1934, **28**, 2725.

[56] Cf. J. F. Durand, *Bull. soc. chim.*, 1935, (5) **2**, 824; *Chem. Abs.*, 1935, **29**, 5820; *Brit. Chem. Abs.* A, 1935, 852.

[57] W. E. Austin, French P. 784,441, 1935; *Chem. Abs.*, 1936, **30**, 110.

[58] W. Schrauth, U. S. P. 1,750,198, March 11, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, **24**, 2216.

PROPERTIES OF THE TERTIARY ALCOHOLS

Dehydration of tertiary alcohols differentiate them even more sharply than do the analogous reactions of secondary alcohols, and it is difficult to distil the former compounds from acid liquors without this decomposition occurring.[59] Also esters of tertiary alcohols are hydrolyzed readily. Due to their structure, oxidation of this type of alcohols cannot lead to the production of aldehydes or ketones of the same number of carbon atoms. The tertiary alcohols are, however, more reactive in such instances as the alkylation of aromatic hydrocarbons, probably because of the ease with which they are dehydrated to the corresponding highly reactive tertiary olefin, which acts as an intermediate.

Some of the physical properties of certain tertiary alcohols are given in Table 98.

TABLE 98.—*Some Higher Tertiary Aliphatic Alcohols.*[60]

Alcohol	Boiling Point °C.	Melting Point °C.	Density 20/4°C.
ter.-Butanol	82.8	25.5	0 789
2-Methylbutanol-2	101.8	−11 9	0.809
2-Methylpentanol-2[a]	122.5		.
2,3-Dimethylbutanol-2	122	−14	0.823
3-Methylpentanol-3	122.6	−22	0 824
2-Methylhexanol-2	142.2		0.816
2,4-Dimethylpentanol-2	130		0 816
2,3,3-Trimethylbutanol-2	132	17	....
2-Ethylpentanol-2	141		0.823
3-Ethylpentanol-3	142		0.840
2,3-Dimethylpentanol-3	140		0.833

[a] F. Beilstein, "Handbuch der Organischen Chemie." 4th Edition, Julius Springer, Berlin, 1918, **1**, 409.

Not only dehydration of tertiary alcohols, but also the converse reaction, i.e., hydration of tertiary olefins, is catalyzed by the presence of acids. Lucas and Liu[61] have studied the comparative effectiveness of a series of acids in promulgating the hydration of such olefins, and report that comparatively dilute acid solutions show considerable catalytic power. Thus, one-tenth molar solutions of several acids tested were found to be efficacious, though activity decreased in the order, dithionic, sulphuric, hydrochloric, hydrobromic, nitric, *p*-toluenesulphonic, picric, oxalic, and acetic acid. Even the weaker organic acids such as formic, oxalic and acetic are known to promote hydration of tertiary olefins in dilute aqueous solution.

Dehydration of tertiary alcohols in the presence of dilute sulphuric acid is a method suggested for the preparation of pure tertiary olefins. Deanesly and Engs[62] report producing pure isobutene by heating the corresponding tertiary alcohol with aqueous sulphuric acid at a temperature of 70° to 85°C., and maintaining the alcohol concentration constant by feeding *ter*-butanol at a rate equivalent to that of olefin formation. Thermal decomposition of *ter*-butyl or *ter*-amyl alcohol appears to be largely dehydration, Schultz and Kistiakowsky[63] find. Experiments conducted using quartz bulbs at 480° to 550°C. indicated the reaction was homogeneous and unimolecular.

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[59] See Chapter 16.

[60] Data from "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1926.

[61] H. J. Lucas and Y-P. Liu, *J.A.C.S.*, 1934, **56**, 2138; *Chem. Abs.*, 1935, **29**, 113; *Brit. Chem. Abs.* **A**, 1934, 1312.

[62] R. M. Deanesly and W. Engs, U. S. P. 2,012,785, Aug. 27, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 6901; *Brit. Chem. Abs.* **B**, 1936, 779.

[63] R. F. Schultz and G. B. Kistiakowsky, *J.A.C.S.*, 1934, **56**, 395, *Chem. Abs.*, 1934, **28**, 2251; *Brit. Chem. Abs.* **A**, 1934, 369.

Polymerization and co-polymerization are important side reactions in the dehydration of the tertiary alcohols. Whitmore and Mixon[64] report that the action of 65 per cent sulphuric acid on an equimolar mixture of tertiary butyl and tertiary amyl alcohols yielded products containing over 69 per cent of polymerized hydrocarbons. Of the latter, 17 per cent were nonenes resulting from condensation of the pentenes and butenes formed during dehydration. They were identified as chemical individuals by ozonolysis and fractionation of the products, and were found to be 1,2,3,3-tetramethylpentene-1 (50 per cent), 3,3,5-trimethylhexene-2 (23 per cent), 2,4,4-trimethylhexene-2 (10 per cent), 2,3,4,4-tetramethylpentene-2 (10 per cent), 2,2,4-trimethylhexene-3 (5 per cent). The two other isomers, 2,4,4-trimethylhexene-1 and 2-ethyl-4,4-dimethylpentene-1, were not found in the products.

Certain tertiary alcohols containing the neopentyl (2,2-dimethylpropyl) group have been found by Whitmore and Laughlin[65] to be readily dehydrated (without rearrangement) under the influence of naphthalene-β-sulphonic acid or iodine. However, in certain cases dehydration is followed by fission and profound isomerization. If 2,2,3,4-tetramethylpentanol-3 is distilled with a small proportion of iodine, it is transformed into 2-isopropyl-3,3-dimethylbutene-1, Nazarov[66] reports. The latter compound, in the presence of 1-bromonaphthalene-4-sulphonic acid, is transformed into 2-methylpropene-1, and 2-methylbutene-2. Treatment of 3-ethyl-2,2,4-trimethylpentanol-3 with iodine yields 4,4-dimethyl-3-isopropylbutene-2, which in turn may be converted by 1-bromonaphthalene-4-sulphonic acid into 2-methylpropene-1, 2-methylpentene-2 and 2-methylpentene-1. This investigator[67] has also observed the dehydration of methyl-di-*ter*-butylcarbinol (2,2,3,4,4-pentamethylpentanol-3) by slow distillation in the presence of iodine. A mixture of olefins was obtained, consisting largely of di-*ter*-butylethylene. This latter compound heated with bromonaphthalenesulphonic acid at 180°C. yielded *ter*-butylethylene, *asym*-methylisopropylethylene, and tetramethylethylene.

Reaction with Aromatics. As previously indicated, tertiary alcohols react vigorously with benzene and benzene homologues under the influence of condensing agents, either those such as strong mineral acids or of the Friedel-Crafts type. The products consist largely of *ter*-alkylated aromatic hydrocarbons. Tzukervanik[68] has noted that compounds of the type $AlCl_2(OR)$ are first formed, and these are decomposed in the presence of excess aluminum chloride or on heating to yield the corresponding olefins and alkyl chlorides. Alkylation is considered by Tzukervanik to proceed according to the consecutive reactions:

$$\begin{aligned} ter\text{-}C_4H_9OH + AlCl_3 &\longrightarrow AlCl_2(OC_4H_9) + HCl \\ AlCl_2(OC_4H_9) &\longrightarrow C_4H_8 + AlCl_2(OH) \\ C_4H_8 + HCl &\longrightarrow C_4H_9Cl \\ C_6H_6 + C_4H_9Cl &\longrightarrow C_6H_5 \cdot C_4H_9 + HCl \end{aligned}$$

By condensing *ter*-butyl or amyl alcohols with benzene or toluene in the presence of aluminum chloride, alkylated hydrocarbons may be obtained in 50 to 70 per cent yields. In this way such compounds as *ter*-amylbenzene, *ter*-amyltoluene, *ter*-butylbenzene and *ter*-butyltoluene were prepared.

Using sulphuric acid as the condensing agent, Barbier[69] reports that isopropylbenzene and *ter*-butyl alcohol furnished isopropyl-*ter*-butylbenzene (boiling at 221°C.). This investigator also reports that a *ter*-butylcymene boiling at 220 to 230°C. may be formed by the reaction between cymene and *ter*-butyl alcohol in the presence of sulphuric acid below 0°C. The product is recovered by diluting the reaction mixture with ice water, separating the hydrocarbon layer, and fractionating.

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[64] F. C. Whitmore and L. W. Mixon. Paper presented before American Chemical Society, Organic Division, San Francisco Meeting, Aug. 19-23, 1935.

[65] F. C. Whitmore and K. C. Laughlin, *J.A.C.S.*, 1933, 55, 3732; *Brit. Chem. Abs.* A, 1933, 1140; *Chem. Abs.*, 1933, 27, 5053.

[66] I. N. Nazarov, *Ber.*, 1936, 69, 18; *Brit. Chem. Abs.* A, 1936, 311. *Ber.*, 1936, 69, 21; *Brit. Chem. Abs.* A, 1936, 311; *Chem. Abs.*, 1936, 30, 2914.

[67] I. N. Nazarov, *Compt. rend. acad. sci. U.R.S.S. (N.S.)*, 1936, 1, 79; *Chem. Abs.*, 1936, 30, 4147.

[68] I. Tzukervanik, *J. Gen. Chem.* (*U.S.S.R.*), 1935, 5, 117; *Chem. Abs.*, 1935, 29, 4746; *Brit. Chem. Abs.* A, 1935, 967.

[69] H. Barbier, *Rev. marques parfum. savon.*, 1934, 12, 325; *Chem. Zentr.*, 1935, 1, 3250; *Brit. Chem. Abs.* A, 1936, 196.

Reaction with Phenols. Tzukervanik and Nazarova[70] find that the condensation of phenols and tertiary alcohols yields largely alkylphenols (and not phenol ethers as in the case of secondary alcohols) while small amounts of olefins and alkylated aromatic hydrocarbons are formed as by-products. *ter*-Butyl alcohol and phenol in light petroleum ether were treated with aluminum chloride to obtain 75 per cent yields of *ter*-butylphenol. Increased amounts of aluminum chloride favored the production of increased quantities of alkylated phenols. As with the benzene homologues, the phenols may be condensed with tertiary alcohols in the presence of strong mineral acids. The products obtained by absorption of olefins in moderately concentrated acid may be directly condensed with phenols, Thomas[71] reports. This investigator prepared *ter*-amylphenol by absorbing *iso*amylene in 62 per cent sulphuric acid, and agitating the resulting liquor for 1 hour with 75 per cent excess of phenol. The oily layer was separated, and refluxed for four hours at 130° to 135°C., then washed with water, neutralized and distilled. Chichibabin[72] noted that the use of phosphoric acid as a condensing agent causes the formation of ortho-alkylated phenols almost exclusively. Using phosphoric acid (*d* 1.83 to 1.85) as a condensing agent, *m*-cresol and *ter*-butyl alcohol yielded *o*-*ter*-butyl-*m*-cresol.[73]

Esters of the Tertiary Alcohols

Esters of tertiary alcohols are not readily produced by direct esterification of the alcohol with carboxylic acids. In the presence of sulphuric acid, for example, the yield of *ter*-butyl acetate from *ter*-butyl alcohol and acetic acid is only about 24 per cent of the theoretical, although better results have been obtained by the use of an aqueous solution of hydrogen sulphide as catalyst. Norris and Rigby[74] reported that good yields could be obtained by refluxing the alcohol with acetic anhydride and a small amount of zinc dust. When treated with acetyl chloride, *ter*-butyl alcohol gives about equal quantities of the acetate and the chloride. However, the acetate is practically the only compound obtained if the acid chloride and alcohol are reacted in the presence of dimethylamine. On the other hand, in the absence of the amine, at temperatures below 20°C., a quantitative yield of the chloride is secured.

Tertiary alkyl esters of organic acids may be prepared by the direct esterification of the appropriate olefin, as described in Chapter 12. However, these esters as yet have found little industrial application, probably because of the ease with which they undergo hydrolysis.

Hughes[75] reported a study of the hydrolysis of *ter*-butyl chloride in aqueous alcohol or acetone. With the alkyl halide in large excess, the velocity of reaction in dilute alkaline solution was constant, and independent of the concentration of alkali, continuing at the same rate even after the alkali was neutralized and the liquid medium became acid. In the presence of a slight excess of potassium hydroxide, the reaction rate is independent of the alkali concentration, and equal to that determined in the complete absence of alkali. In dilute solutions, the reaction velocity is independent of the concentration of the alkyl halide, but at higher concentrations its value shows a marked increase. In ethyl alcohol solutions, the presence of water has a very strong influence. In 90 per cent ethanol the value of the reaction constant is 0.00616, but in 40 per cent ethanol it rises to 4.66. Temperature, too, greatly affects the rate of dissociation. In 80 per cent ethyl alcohol the value of the constant increases from 0.0031 at 8°C. to 0.380 at 45°C.

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[70] I. Tzukervanik and Z. Nazarova, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 767; *Chem. Abs.*, 1936, **30**, 443. See also R. C. Huston and T. Y. Hsieh, *J.A.C.S.*, 1936, **58**, 439; *Chem. Abs.*, 1936, **30**, 2939.

[71] C. A. Thomas, British P. 420,636, 1934, to Sharples Solvents Corp.; *Chem. Abs.*, 1935, **29**, 3351; *Brit. Chem. Abs.* **B**, 1935, 140.

[72] A. E. Chichibabin, *Bull. soc. chim.*, 1935, (5) **2**, 497; *Brit. Chem. Abs.* **A**, 1935, 614; *Chem. Abs.*, 1935, **29**, 3660.

[73] A. E. Chichibabin, French P. 775,875, 1935; *Chem. Abs.*, 1935, **29**, 2976.

[74] J. F. Norris and W. Rigby, *J.A.C.S.*, 1932, **54**, 2088; *Brit. Chem. Abs.* **A**, 1932, 718; *Chem. Abs.*, 1932, **26**, 3229.

[75] E. D. Hughes, *J.C.S.*, 1935, 255; *Chem. Abs.*, 1935, **29**, 2928; *Brit. Chem. Abs.* **A**, 1935, 452.

Carre and Libermann[76] state that the alkyl chlorosulphites (of the formula ROSOCl) may be prepared by adding the alcohol to a 10 to 20 per cent excess of thionyl chloride, and allowing the mixture to stand at room temperature for 48 hours. Although the *sec*-butyl chlorosulphite was prepared and distilled, the *ter*-butyl compound was too unstable to permit of distillation.

French, McShan and Johler[77] observed that treatment of tertiary bromides with hydroxides of silver, barium or those of the alkali metals yielded only small proportions of olefins, alcohol being the main product. Woodburn and Whitmore[78] state that the tertiary halides are more resistant to hydrolysis than is ordinarily supposed. Although the tertiary chlorides with hot water or hot sodium carbonate solution yield the corresponding olefin exclusively, with cold water or cold sodium carbonate, a certain amount of tertiary alcohol is formed together with the unsaturated hydrocarbon. The physical properties of some of the *ter*-butyl esters are listed in Table 99.

TABLE 99.—*Tertiary Butyl Esters.*

Compound	Boiling Point °C.	Density (d^{25}_4)
ter-Butyl chloride.............	51.0	0.8370
ter-Butyl acetate.............	97.8	0.8593
ter-Butyl benzoate............	96(at 2 mm.)	0.9928
ter-Butyl propionate..........	120-121	0.8647(d^{20}_4)
ter-Butyl methoxyacetate[a]....	62-64(at 22 mm.)	0.9563(d^{20}_4)

[a] M. H. Paloma, E. J. Salmi, J. I. Jansson and T. Salo, *Ber.*, 1935, **68**, 303; *Chem. Abs.*, 1935, **29**, 2907; *Brit. Chem. Abs.* **A**, 1935, 473

ETHERS OF TERTIARY ALCOHOLS

According to Norris and Rigby,[79] the mixed ethers of tertiary alcohols, such as *ter*-butanol, may be prepared in fairly good yield, using sulphuric acid or aqueous sodium hydrogen sulphate as catalyst. These investigators added one mole of the tertiary alcohol to a boiling mixture of two moles of ethyl alcohol and a 15 per cent solution of sulphuric acid, the volume of which was about two and a half times that of the ethyl alcohol. The minimum boiling mixture of the ether and water was distilled from the reaction mixture. A yield of 95 per cent of the mixed ether was reported. The reaction of *ter*-butanol with a secondary alcohol (isopropanol) required a different catalyst, since the alcoholic hydrogen of secondary alcohols, as already indicated, is less reactive than that of the primary carbinols. Therefore, a greater molecular proportion of isopropyl alcohol was employed, and as catalyst, sodium hydrogen sulphate was employed instead of the acid, in order to prevent formation of isobutene by dehydration of the *ter*-butanol. In this way a yield of 82 per cent of *ter*-butyl-*sec*-propyl ether was obtained.

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[76] P. Carre and D. Libermann, *Bull. soc. chim.*, 1933, **53**, 1050; *Chem. Abs.*, 1934, **28**, 1658.

[77] H. E. French, W. H. McShan and W. W. Johler, *J.A.C.S.*, 1934, **56**, 1346; *Chem. Abs.*, 1934, **28**, 4372; *Brit. Chem. Abs.* **A**, 1934, 866.

[78] H. M. Woodburn and F. C. Whitmore, *J.A.C.S.*, 1934, **56**, 1394; *Brit. Chem. Abs.* **A**, 1934, 866; *Chem. Abs.*, 1934, **28**, 4375.

[79] J. F. Norris and G. W. Rigby, *loc. cit.*

It was found that these tertiary ethers are highly reactive. When *ter*-butylethyl ether was allowed to stand in contact with concentrated hydrochloric acid, the former was rapidly converted (to the extent of 99 per cent) into *ter*-butyl chloride. The reactivity of the tertiary ether as compared to the corresponding normal ether is illustrated by the time of reaction of the two ethers with hydrochloric acid. The normal butylethyl ether reacts with hydrochloric acid to give a 25 per cent conversion in 768 hours at 25°C. The tertiary ether corresponding gives a 25 per cent yield of *ter*-butyl chloride in 0.83 hour, at 0°C.

Evans and Edlund[80] report a method of producing the tertiary ethers of polyhydric alcohols such as ethylene glycol by the reaction of the corresponding olefin with the alcohol. Mineral acids, or metallic salts serve as catalysts. These investigators find that in general the tertiary alkyl ethers of monohydric alcohols are relatively insoluble in water, form peroxides only slowly, and are stable in alkaline but not in acid solutions. Those derived from polyhydric alcohols are relatively soluble in water. These ethers have been suggested as entraining agents, solvents or diluents in lacquer and varnish preparations.[81]

The physical properties of some of the mixed tertiary ethers, as given by Evans and Edlund, are listed in Table 100.

TABLE 100.—*Mixed Tertiary Alkyl Ethers.*

Ether	Boiling Point, °C.	d_4^{20}
Methyl *ter.*-butyl	55	0.7405
Ethyl *ter.*-butyl	73	0.7404
Isopropyl *ter.*-butyl	87-88	0.742
n-Butyl ter.-butyl	123-124	0.7615
Isobutyl *ter.*-butyl	114	0.7516
sec.-Butyl *ter.*-butyl	114-115	0.7604
Isoamyl *ter.*-butyl	138-140	0.7662
Methyl *ter.*-amyl	86-87	0.7703
Ethyl *ter.*-amyl	101-102	0.7657
Isopropyl *ter.*-amyl	114-115	. . .
Methyl *ter.*-hexyl	113	0.7815
ter.-Monobutyl ether of ethylene glycol	153	0.8970
ter.-Dibutyl ether of ethylene glycol	171	0.8266
Mixed methyl *ter.*-butyl ether of ethylene glycol	131-132	0.8399
Mixed ethyl *ter.*-butyl ether of ethylene glycol	148	0.8311
Mixed *n*-butyl *ter.*-butyl ether of ethylene glycol	83 (20 mm.)	0.8317
ter.-Monobutyl ether of 1,2-propene glycol	151-153	0.8707
ter.-Monobutyl ether of glycerol	93-94 (5 mm.)	0.9947
ter.-Dibutyl ether of glycerol	80-82 (4 mm.)	0.8921
ter.-Monoamyl ether of ethylene glycol	50-55 (3 mm.)	0.8993
ter.-Monobutyl ether of diethylene glycol	72 (2 mm.)	0.9374
Phenyl *ter.*-butyl	185-186	0.9214
Benzyl *ter.*-butyl	82-83 (8 mm.)	0.921

USES OF TERTIARY BUTYL ALCOHOL

Ellis[82] has pointed out the applicability of *ter*-butyl alcohol in solvent refining processes to free oils of wax and asphalt. Thus, a pressing distillate obtained from a Pennsylvania crude oil was mixed at room temperature with half its volume of *ter*-butyl alcohol. The mixture was then cooled to 5-10°C. On remaining at this temperature for some time, a voluminous precipitate was formed, consisting principally of wax, which could be separated from the alcohol-oil solution by filtration. The clear filtrate was further separated into oil and alcohol by distillation. A quantity of heavy bottoms (obtained by the distillation of a Mid-Continent crude oil to about 20 per cent of bottoms), containing both wax and asphalt was mixed with *ter*-butyl alcohol. An alcohol-oil ratio of about 5 to 1 was used with this heavy material, and the mixture was heated to 35-40°C. to secure complete solution of the oil in the alcohol. During heating the mixture was well agitated. The asphaltic content did not entirely dissolve under these conditions, but some separated in the form of small globules which coalesced, particularly on cooling, to form a tarry mass. The alcohol containing the oil was decanted after cooling to somewhat below room temperature. The alcohol solution was further cooled to 5-10°C. to precipitate wax, and the alcohol and oil separately recovered by distillation.

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[80] T. W. Evans and K. R. Edlund, *Ind. Eng. Chem.*, 1936, **28**, 1186.

[81] K. R. Edlund and T. Evans, British P. 393,753, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1933, **27**, 5752; *Brit. Chem. Abs.* B, 1933, 822.

[82] Carleton Ellis, U. S. P. 2,062,355, Dec. 1, 1936 to Standard Oil Development Co.; *Chem. Abs.*, 1937, **31**, 849. See also British P. 450,511, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1937, **31**, 249; French P. 801,026, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1937, **31**, 250.

The cooling step may be carried to a lower temperature, if desired, to secure further separation of wax. However, if the temperature is made too low, the rather easily frozen *ter*-butyl alcohol will solidify. This is not harmful, it is said, unless carried to an extreme, as a slight deposit of alcohol crystals may serve as an aid in forming a filtering network of crystals. The separation of the mixed alcohol and wax crystals may be brought about by allowing the material to warm up to the melting point of the alcohol and filtering off the wax.

By the addition of a small quantity (5 per cent) of water to a solvent composed of 80 per cent *ter*-butyl alcohol and 20 per cent *ter*-amyl alcohol, separation can be made to occur when the solution is cooled. When a Colombian lubricating distillate was treated with this mixed solvent, and heated to 65-70°C. and at the same time thoroughly agitated, solution took place. However, when the batch was permitted to cool to room temperature, a sharp separation occurred, forming two layers. The lower (oil) layer was withdrawn, and the dissolved solvent separated by distillation. Distillation of the upper layer permits separation of the alcohol and extract.

A mixture of propene chloride and *ter*-butyl alcohol has been proposed as a solvent for cellulose acetate. Taylor[83] states that a composition containing these substances can be used in forming flexible sheets of cellulose acetate.

Parks, Warren and Greene[84] have found that *ter*-butyl alcohol may be used satisfactorily in molecular weight determinations by the Beckmann freezing point method. The hygroscopic character of the solvent and its tendency to undercool must be taken into consideration in the manipulations, but these difficulties may be overcome by using a freezing tube stopped against moisture from the air by means of rubber tubes. Undercooling was overcome by sealing a small platinum wire into the lower end of the tube. When making determinations, this wire was touched from time to time with a soldering copper which had been cooled on solid carbon dioxide, giving a small deposit of crystals on the surface of the wire from which crystallization would proceed.

The alcohol with which the work was done was a commercial product (originally freezing at 20°C.) which had been fractionally distilled twice over lime and was then subjected to ten fractional crystallizations. The final product melted at 25.4°C. By thermodynamic calculations the cryoscopic constant was determined as approximately 8.27. Experimental work on freezing mixtures in dilution such as to lower the freezing point of the mixture by one degree gave the cryoscopic constant $K = 8.30$ in the equation

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[83] E. R. Taylor, U. S. P. 2,000,622, May 7, 1936, to Eastman Kodak Co.; *Chem. Abs.*, 1936, **30**, 4175; *Brit. Chem. Abs.* **B**, 1936, 588.

[84] G. S. Parks, G. E. Warren and E. S. Greene, *J.A.C.S.*, 1935, **57**, 616; *Brit. Chem. Abs.* **A**, 1935, 699; *Chem. Abs.*, 1935, **29**, 3217.

$$M = 1000\,K(g/G\Delta T_f)$$

where M is the molecular weight of the solute, K the cryoscopic constant of the solvent, g the number of grams of solute in solution, G the number of grams of solvent, and ΔT_f the difference between the original freezing point of the *ter*-butyl alcohol (25.4°C.) and the freezing point of the particular solution being tested.

The experimental values for the molecular weights of various solutes were determined with reasonably satisfactory accuracy except in the cases of isopropyl alcohol (error of +23.1 per cent), *sec*-butyl alcohol (+16.5 per cent), *ter*-amyl alcohol (+90.9 per cent), phenol (−3.7 per cent) and *p*-toluidine (−4.7 per cent). In the case of phenol, the observed error may be due to the formation of a compound with the alcohol. The *p*-toluidine on the other hand was not entirely pure. In the cases of the three alcohols, it was shown that mixed crystals were being formed. The equation given above does not apply in the latter instance which is, apparently, the source of anomalous results. However, the method was found applicable to all classes of hydrocarbons, and most types of organic compounds, including the primary alcohols. (With ethylbenzene, the percentage error was −0.4 per cent. With *o*-xylene, no error was found.)

One of the most important reactions of the tertiary alcohols involves their condensation with phenols and benzene derivatives in the presence of a condensing agent such as aluminum chloride, zinc chloride, or phosphoric or sulphuric acid. A tertiary alkyl phenol may be prepared, thus, by reacting *ter*-butyl alcohol with phenol in the presence of aluminum chloride at about 30°C.[85] Langwell[86] reports a similar condensation using zinc chloride as the condensing agent. He proposes, however, that the temperature of the reaction can be controlled by having present a volatile liquid which boils at a temperature somewhat lower than the operating temperature (about 130°C. in case of tertiary alcohols. A similar condensation of primary alcohols requires a temperature of 180°C.) Interaction may be effected by adding the volatile liquid (e.g., isohexene or benzene), phenol, and alcohol to a solution of zinc chloride, and heating under reflux. Chichibabin[87] used phosphoric acid in effecting combination of *ter*-butyl alcohol and *o*-cresol. The alcohol, *o*-cresol and phosphoric acid were heated together at 50°C. to produce *o*-*ter*-butyl-*m*-cresol. Maschmeijer and Takens[88] reacted *m*-cresol methyl ether with *ter*-butyl alcohol in 2 to 4 times its volume of sulphuric acid of 85 to 95 per cent strength at lower temperatures (20°C. or less) to obtain 1-methyl-3-methoxy-4-*ter*-butylbenzene. Barbier[89] states that very little sulphonation takes place in the alkylation of cymene with *ter*-butyl alcohol in the presence of sulphuric acid if the temperature is kept below 0°C. Afterwards, separation of the reacted compounds may be obtained by adding ice water, to form an oily layer containing the *ter*-butylcymene. The latter substance may be recovered by fractionating the products and collecting the portion boiling at 220° to 230°C. It is said that a good yield of a material which is entirely nitratable to dinitro-*ter*-butylcymene is obtained.

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[85] R. C. Huston, U. S. P. 2,051,300, Aug. 18, 1936, to Mich. State Board of Agriculture; *Chem. Abs.*, 1936, **30**, 6761.

[86] H. Langwell, British P. 424,506, 1935, to British Industrial Solvents Ltd.; *Brit. Chem. Abs.* B, 1935, 443; *Chem. Abs.*, 1935, **29**, 4376. See also H. Langwell and E. E. Connolly, British P. 425,373, 1935; *Brit. Chem. Abs.* B, 1935, 443; *Chem. Abs.*, 1935, **29**, 5458. French P. 778,890, 1935; *Chem. Abs.*, 1935, **29**, 4855; H. Langwell and C. B. Maddocks, U. S. P. 2,031,719, Feb. 25, 1936; *Chem. Abs.*, 1936, **30**, 2200.

[87] A. E. Chichibabin, *Bull. Acad. Sci. (U.R.S.S.)*, 1935, 951; *Brit. Chem. Abs.* A, 1936, 602. See also A. E. Chichibabin, French P. 775,875, 1935; *Chem. Abs.*, 1935, **29**, 2976.

[88] A. J. H. Maschmeijer and E. Takens, U. S. P. 2,038,947, April 28, 1936, to A. Maschmeijer Jr., Inc.; *Chem. Abs.*, 1936, **30**, 4181.

[89] H. Barbier, U. S. P. 1,951,123, March 13, 1934; *Chem. Abs.*, 1934, **28**, 3426; *Brit. Chem. Abs.* B, 1935, 182.

Van Schaack[90] states that a mixture of 30 volumes of *ter*-butyl alcohol and 70 volumes of gasoline displayed better antiknock properties than did a 30-70 blend of benzol and gasoline. The use of the butyl alcohol in this manner is said to have advantages over the analogous utilization of ethanol, in that the four-carbon-atom alcohol has a higher fuel value, while its boiling point and volatilization characteristics closely resemble those of the lighter alcohol (ethanol). Deanesly[91] has proposed that the alcohols formed by absorbing olefins in sulphuric acid be extracted in an organic solvent immiscible with the acid, and the solution of alcohols so produced used directly as an antiknock fuel, or as a solvent. It has been suggested that *ter*-butyl alcohol alone be used as a fuel for racing motor cars or airplane engines. In such instances it may be mixed with as much as 30 per cent water, or may contain polymers of olefins, for example the dimer of 2-methylpropene, the dehydration product of *ter*-butanol.[92]

Birch, Pim and Tait[92a] suggest that the high antiknock value of isoolefins may be accounted for indirectly through the medium of tertiary alcohols. They find that the action of concentrated sulphuric acid on a mixture of tertiary amyl and butyl alcohols (derived from the corresponding lower olefins) gives good yields of the polymers. 2,2,4-Trimethylpentane, the octane commonly employed in octane rating, was produced by this type of condensation and subsequent hydrogenation. Several other fractions were obtained showing octane ratings as high as 98 to 100.2.

In numerous applications, particularly in producing blended fuel containing the alcohol, a dry *ter*-butyl alcohol is desirable. Hartmann[93] finds that liquids of this character may be rendered anhydrous by distillation with phthalic anhydride. He observes that the anhydride combines preferentially with water and any primary butanol that may be present, while the tertiary alcohol may be recovered by distillation. The resulting phthalic acid may be dehydrated and reused.

Becker and Muller[94] report that wetting, frothing and emulsifying agents may be produced from tertiary alcohols by treatment with concentrated sulphuric acid. In the suggested process, 500 parts of tertiary alcohol (e.g., *ter*-butanol) are mixed with 500 parts of concentrated sulphuric acid, while cooling. The mixture is then heated on a water bath, and in the course of two hours, separation occurs. The oily layer is withdrawn and reacted with a strong sulphonating agent, such as chlorosulphonic acid. The resulting sulphonated polymerized hydrocarbons are said to have wetting properties, either when used as the sulphonic acids or in the form of their sodium salts.

USES OF TERTIARY ESTERS AND ETHERS

Norris and Rigby[95] state that reaction between *ter*-butyl alcohol and concentrated hydrochloric acid proceeds more than 200,000 times as rapidly as that between the primary alcohol and the acid. It appears from their work that the hydroxyl group of the tertiary alcohols is much more reactive than that of the primary or even secondary alcohols. The alcoholic hydrogen, however, is not as reactive as that of the corresponding atom in the normal butanol. For example, metallic sodium and *ter*-butyl alcohol interact slowly and the sodium *ter*-butylate formed combines very slowly with alkyl halides to give ethers. When the tertiary alkyl halides are treated with sodium derivatives of normal alcohols, the result is mainly the elimination of hydrogen chloride from the tertiary halide.

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[90] R. H. Van Schaack. U. S. P. 1,907,309, May 2, 1933, to Van Schaack Bros. Chem. Works, Inc.; *Brit. Chem. Abs.* B, 1934, 184; *Chem. Abs.*, 1933, **27**, 3587.

[91] R. M. Deanesly, U. S. P. 2,042,212, May 26, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 4870. See also E. C. Williams and G. H. van de Griendt, Canadian P. 347,900, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 3071

[92] French P. 798 378, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 7312.

[92a] S. F. Birch, F. B. Pim and T. Tait, *J.S.C.I*, 1936, **55**, 335T.

[93] W. W. Hartman, U. S. P. 1,950,889, March 13, 1934, to Eastman Kodak Co.; *Chem. Abs.*, 1934, **28**, 3425; *Brit. Chem. Abs.* B, 1935, 138.

[94] L. Becker and R. Muller, U. S. P. 1,950,287, March 6, 1934; *Chem. Abs.*, 1934, **28**, 3626; *Brit. Chem. Abs.* B, 1935, 93.

[95] J. F. Norris and G. W. Rigby, *J.A.C.S.*, 1932, **54**, 2088; *Chem. Abs.*, 1932, **26**, 3229; *Brit. Chem. Abs.* A, 1932, 718.

Deanesly,[96] however, has reported that the tertiary alkyl hypohalites can be prepared by a direct process. Equimolar proportions of the alcohol (e.g., *ter*-butanol) and sodium hydroxide are treated with the halogen (bromine or chlorine) in the presence of sufficient water to form a two-phase system.

Putnam, Britton and Perkins[97] describe the condensation of tertiary alkyl halides with phenols in the presence of aluminum chloride. Thus, they observe that *p*-*ter*-butylphenol may be formed by the interaction of a phenol (having the para-position free) and *ter*-butyl chloride at a temperature between 20 and 50°C. in the presence of aluminum chloride. A liquefying solvent such as phenol which will not unite with the substances involved to form undesirable by-products is said to aid the reaction. Perkins, Dietzler and Lundquist[98] used an analogous reaction for the preparation of 2,4-di-*ter*-butylphenol as well as the 4-*ter*-butylphenol and a small yield of 2-*ter*-butylphenol. Thus, if *ter*-butyl chloride is heated with an equimolar amount of phenol and 0.5 per cent of aluminum chloride at 90°C., 70.2 per cent of 4-*ter*-butylphenol, 7.1 per cent of 2,4-di-*ter*-butylphenol and 1.2 per cent of 2-*ter*-butylphenol are obtained.

Evans and Edlund[99] suggested the employment of mixed tertiary ethers in extracting and concentrating various organic carboxylic acids. They propose that such acids as formic, acetic, propionic or butyric could be freed from inorganic acid content by azeotropic distillation with methyl-*ter*-amyl ether, methyl-*ter*-butyl ether, or a homolog. The ether should be so chosen that it boils at a temperature higher than the boiling point of the acid under treatment.

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[96] R. M. Deanesly, U. S. P. 1,938,175, Dec. 5, 1933, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 1053; *Brit. Chem. Abs.* **B**, 1934, 824.

[97] M. E. Putnam, E. C. Britton and R. P. Perkins, U. S. P. 2,039,344, May 5, 1936, to Dow Chemical Co.; *Chem. Abs.*, 1936, **30**, 4176.

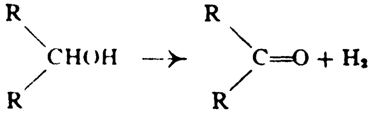
[98] R. P. Perkins, A. J. Dietzler and J. T. Lundquist, U. S. P. 1,972,599, Sept. 4, 1934, to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1935, 716; *Chem. Abs.*, 1934, **28**, 6532.

[99] T. Evans and K. R. Edlund, British P. 431,313, 1934, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1935, 796; *Chem. Abs.*, 1935, **29**, 8005.

Chapter 18

Production, Properties and Uses of Ketones Derived from Alcohols and from Hydrocarbons

The lower aliphatic ketones, particularly acetone and methyl ethyl ketone, find application in many branches of chemical technology, notably as solvents and as raw materials in the synthesis of organic chemicals and resins. Both saturated and unsaturated hydrocarbons may be converted into ketones by several types of single-stage process which do not involve the intermediate formation of alcohols. In general, however, ketones are produced from secondary alcohols through the removal of two atoms of hydrogen from the latter either by dehydrogenation or by oxidation. This may be represented by



$$R_2CHOH \longrightarrow R_2C{=}O + H_2$$

where *R* represents an alkyl or cycloalkyl group.[1]

PRODUCTION OF KETONES FROM SECONDARY ALCOHOLS

The conversion of secondary alcohols, such as isopropanol, into ketones involves a reversible endothermic reaction, high temperatures favoring ketone formation. Dehydrogenation is said to be rapid at temperatures of 300°C. or above when catalysts are employed. However, the reaction may also be carried out exothermally in the presence of air or oxygen. A combination of the endothermic dehydrogenation with the exothermic oxidation process is suggested in certain instances to obtain better temperature control. Various catalysts have been proposed for the two types.

Contact agents for vapor-phase dehydrogenation of secondary alcohols at elevated temperatures include copper, lead, metallic sulphides, and the phosphides, selenides, tellurides, antimonides, arsenides and bismuthates of zinc, cadmium, nickel, cobalt, iron, aluminum, calcium and magnesium. Recommended temperatures range from 150° to 625°C.[2] A reported disadvantage in this type of reaction is the rapid deterioration of many of the catalysts on prolonged use, with consequent necessity for revivification. Also, the simultaneous occurrence of side reactions, principally dehydration of the alcohol to the corresponding olefin, reduces the efficiency of ketone formation. It is reported that certain copper alloys are superior to copper as regards length of usefulness and selective action. For example, employment of copper-zinc alloys, e.g., brass, with a reaction temperature of 370-430°C. is proposed by De Simo.[3] Metallic rhenium has been suggested as a contact agent for the dehydrogenation of isopropanol.[4] It was said that dehydrogenation of the alcohol at 400°C. furnished 85 per cent of the theoretical amount of acetone. Further, it was stated that decomposition of the ketone was inhibited by this catalyst.

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[1] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. For a review of the technical aspects of industrial solvents, see T. H. Durrans, *J.S.C.I.*, 1935, **44**, 585; *Brit. Chem. Abs.* B, 1935, 714; *Chem. Abs.*, 1935, **29**, 5541.

[2] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. Copper was one of the first catalysts proposed for this type of dehydrogenation. (See Carleton Ellis, *loc. cit.*) The catalytic activity of the metal in this respect is discussed by W. G. Palmer, *Proc. Roy. Soc. London*, 1921, **99A**, 412; *Chem. Abs.*, 1921, **15**, 3923; *J.C.S.*, 1921, **120** (2), 542.

In some cases promoters are advocated for use in conjunction with catalysts. For example, in the preparation of acetone, isopropanol may be contacted at 300°C. with reduced copper on pumice and a promoter, consisting of an oxide of zinc, thorium, cerium or zirconium.[5] Lazier[6] has advocated a difficultly reducible oxide of a dehydrogenating metal (e.g., zinc oxide) to be employed as a promoter in conjunction with copper and cadmium chromites.

The dehydrating effect of such oxides as those of zinc or uranium is said to be suppressed by incorporation of a more acidic oxide or salt. For example. zinc oxide alone is said to convert isopropanol into acetone in 95 per cent yield at 400°C., but when 7 per cent of zinc sulphate is admixed with the above contact agent, the yield is raised to 99 per cent.[7]

Use of a water-soluble salt of an alkali metal, e.g., sodium carbonate or silicate, as a carrier for the dehydrogenation catalyst is said to inhibit dehydration to olefins.[8]

Liquid-phase dehydrogenation of isopropyl alcohol to acetone employing 2 to 750 atmospheres pressure and temperatures of 200-500°C. has been proposed.[9] A catalyst of chromium oxide together with the oxides of manganese or zinc is advocated. Also, it has been suggested to carry out this type of dehydrogenation in the presence of an aromatic hydrocarbon which will undergo hydrogenation during the process.[10] For example, isopropanol is heated to 250°C. under a pressure of 300 lbs. in a solution of nickel carbonate and benzene.

Catalytic oxidation of secondary alcohols with the aid of such substances as copper and silver has been frequently described, but one of the reported disadvantages is the difficulty of controlling the reaction temperature. This is a result of the exothermic nature of the oxidation as was mentioned previously. Cardarelli[11] has pointed out that the conversion of isopropanol to acetone may be effected by conducting a mixture of the alcohol and the theoretical amount of oxygen over a catalyst, such as copper, at 225-350°C. Temperature control is accomplished by employing as an exterior cooling medium a stable organic compound boiling between 225-350°C., e.g., diphenylmethane, biphenyl, diphenyl ether or naphthylamine. Further, the gases which leave the reaction chamber are employed to preheat the entering isopropanol and oxygen to the reaction temperature. See

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[3] M. De Simo. U. S. P. 1,952,702, Mar. 27. 1934, to Shell Development Co.; *Brit. Chem. Abs.* B, 1935, 139; *Chem. Abs.*, 1934, **28**, 3418. Also, Canadian P. 339,529, 1934; *Chem. Abs.*, 1934, **28**, 2724. British P. 392,652, 1933, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* B, 1933, 776; *Chem. Abs.*, 1933, **27**, 5337.

[4] M. S. Platonov, S. B. Anisimov and V. M. Krasheninnikova, *Ber.*, 1936, **69**, 1050; *Chem. Abs.*, 1936, **30**, 4812; *Brit. Chem. Abs.* A, 1936, 820.

[5] H. F. J. Lorang, U. S. P. 2,039,543, May 5, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 4180.

[6] W. A. Lazier, U. S. P. 1,895,516, Jan. 31, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1933, 905; *Chem. Abs.*, 1933, **27**, 2455.

[7] H. S. Taylor and W. A. Lazier, U. S. P. 1,895,529, Jan. 31, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1933, 905; *Chem. Abs.*, 1933, **27**, 2455.

[8] A. J. van Peski and H. F. J. Lorang, U. S. P. 1,956,088, April 24, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 4067; *Brit. Chem. Abs.* B, 1935, 182.

[9] W. A. Lazier, U. S. P. 1,999,196, April 30, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 4022.

[10] British P. 404,643, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1934, 267.

[11] E. J. Cardarelli, U. S. P. 1,988,481, Jan. 22, 1935, to Standard Alcohol Co.; *Chem. Abs.*, 1935, **29**, 1431; *Brit. Chem. Abs.* B, 1936, 89. See also E. C. Wagner, *J. Chem. Education*, 1934, **11**, 309; *Chem. Abs.*, 1934, **28**, 3973.

Fig. 108. On the other hand, Woolcock[12] produced acetone by oxidation of an azeotropic mixture of isopropanol and water with air. In the procedure, 63.5 g. of the binary mixture are conducted, together with 1.78 cu. ft. of air, over silver gauze. During the time of contact the reactants are maintained at 656°C.

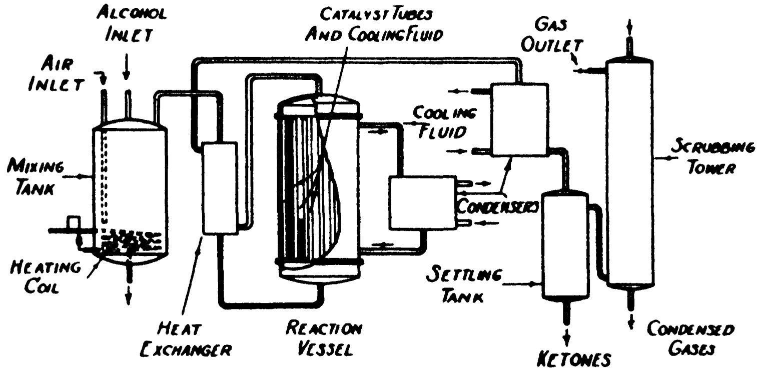

FIG. 108.—Diagram of Apparatus for Catalytic Oxidation of Secondary Alcohols to Ketones. (E. J. Cardarelli)

PRODUCTION OF KETONES FROM PRIMARY ALCOHOLS AND THEIR DERIVATIVES

A number of processes have been developed whereby primary alcohols, such as ethanol, as well as certain derivatives of such alcohols (including aldehydes, ethers and esters) are converted into ketones by catalytic treatment, usually in the vapor phase, at high temperatures.

The mechanism of the conversion of ethanol into acetone by reaction with steam has been examined by Kagan and his co-workers,[13] who consider that ethyl acetate is an important intermediate in the chain of reactions involved. In the absence of steam, ethyl acetate is formed from ethyl alcohol by catalytic dehydrogenation at 300-350°C.

$$2C_2H_5OH \longrightarrow 2CH_3CHO + 2H_2$$
$$2CH_3CHO \longrightarrow CH_3COOC_2H_5$$

The anhydrous ester in the presence of zinc oxide and chromic oxide at 400°C. is converted into acetone, ethanol, ethylene and carbon dioxide. If steam is admixed with the original reactants, acetic acid tends to result in place of the ester. In the latter instance at temperatures above 400°C. acetone is formed instead of acetic acid. Hydration of ethyl ether to ethanol and the subsequent conversion to acetone in 40 to 50 per cent yield are said to take place when the ether is mixed with 3 to 5 volumes of steam and passed at 400 to 500°C. over a catalyst of mixed oxides of aluminum, iron and magnesium.[14] A 96 per cent yield of acetone from acetaldehyde is stated to be secured from the passage of the aldehyde over an iron oxide-manganese oxide mixture at 400°C.[15] The chain of processes by which ethanol, diethyl ether, acetaldehyde and ethyl acetate are converted into acetone by catalytic decomposition in the presence of steam is represented by Kagan and his collaborators as follows:

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[12] J. W. Woolcock, U. S. P. 2,015,094, Sept. 24, 1935, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1935, **29**, 7346.

[13] M. Ya. Kagan, I. A. Sobolev and G. D. Lyubarskii, *Ber.*, 1935, **68**, 1140; *Brit. Chem. Abs.* **A**, 1935, 963; *Chem. Abs.*, 1935, **29**, 6207.

[14] M. Ya. Kagan, I. M. Rossinskaya and S. M. Cherntzov, *J. Gen. Chem.* (*U.S.S.R.*), 1933, **3**, 337; *Brit. Chem. Abs.* **A**, 1933, 1252; *Chem. Abs.*, 1934, **28**, 2323.

[15] N. D. Zelinskii, M. I. Ushakov, B. M. Mikhailov and Yu. A. Arbuzov, *J. Chem. Ind.* (*Moscow*), 1933, No. 7, 63; *Brit. Chem. Abs.* **B**, 1934, 52; *Chem. Abs.*, 1934, **28**, 1015.

$$\begin{aligned} 2C_2H_5OC_2H_5 + 2H_2O &\longrightarrow 4C_2H_5OH \longrightarrow 4CH_3CHO + 4H_2 \\ 4CH_3CHO &\longrightarrow 2CH_3COOC_2H_5 \xrightarrow{2H_2O} 2CH_3COOH + 2C_2H_5OH \\ 2CH_3COOH &\longrightarrow CH_3COCH_3 + CO_2 + H_2O \end{aligned}$$

The overall effect in the case of ethanol may be expressed by the equation:

$$2C_2H_5OH + H_2O \longrightarrow CH_3COCH_3 + CO_2 + 4H_2$$

A number of contact agents have been suggested for promoting the conversion of ethanol or acetaldehyde into acetone by reaction with steam at temperatures up to 500°C. and at atmospheric pressure. The proposed catalysts include the following:

1. A mass containing porous carbon and oxides of zinc, cadmium, manganese or iron.[16]
2. Tin oxide and an oxide of a rare-earth metal, such as cerium.[17]
3. Oxides of metals which are capable of forming isomorphous[18] carbonates. Thus, the alcohol is led over a mixture of iron oxide and calcium carbonate, both deposited on a carrier of iron.[19]
4. An oxide of iron mixed with either nickel or cobalt oxide.[20]
5. Oxygen compounds of nickel (e.g., nickel acetate) with a carrier of oxidized spongy iron, the nickel content not exceeding 20 per cent of the total mass.[21]
6. A mixture of zinc oxide and calcium silicate.[22]
7. A hard cement, produced by treating oxygen compounds of zinc and calcium with water. Such compounds may be prepared by heating calcium and zinc hydroxides with air at 1500°C.[23]
8. Calcium silicate, borate or phosphate.[24]
9. A composite of iron and manganese oxides together with barium carbonate.[25]
10. A mixed-oxide of zinc and chromium, incorporated with a metal halide.[26]

Kagan[27] reports the production of acetone by passage of a mixture of steam and diethyl ether at 400-500°C. over a mixture of metallic oxides, such as those just mentioned.

Also, the direct conversion of vaporized ethanol into acetone in the absence of steam has been suggested. The partial pressure of the alcohol is maintained at less than 1 atmosphere, and temperatures of the order of 400 to 500°C. are employed. The proposed catalysts include oxides of chromium, manganese, copper and iron[28] and a mixture of zinc oxide with ferric or zinc chloride.[29]

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[16] H. Walter, German P. 622,493, 1935, to Deutsche Gold und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1936, **30**, 1394.

[17] H. Meerwein and H. Morschel, U. S. P. 1,891,333, Dec. 20, 1932, to Schering-Kahlbaum A.-G.; *Brit. Chem. Abs.* **B**, 1934, 10; *Chem. Abs.*, 1933, **27**, 1896.

[18] Isomorphism is a term employed to connote the fact that analogous elements can replace one another in compounds without affecting the apparent shape of the crystals.

[19] K. Roka, U. S. P. 1,944,109, Jan. 16, 1934, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1934, **28**, 2019; *Brit. Chem. Abs.* **B**, 1934, 920. U. S. P. 1,936,118, Nov. 21, 1933; *Chem. Abs.*, 1934, **28**, 779.

[20] W. Querfurth, U. S. P. 1,961,912, June 5, 1934, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1934, **28**, 4744.

[21] W. Querfurth, U. S. P. 2,002,794, May 28, 1935, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1935, **29**, 4772.

[22] H Dreyfus, U. S. P. 1,965,072, July 3, 1934; *Chem. Abs.*, 1934, **28**, 5469.

[23] H. F. Oxley, W. A. Groombridge and E. B. Thomas, U. S. P. 1,954,023, April 10, 1934, to Celanese Corp. of America; *Chem. Abs.*, 1934, **28**, 3741.

[24] H. Dreyfus, U. S. P. 1,949,412, Mar. 6, 1934; *Chem. Abs.*, 1934, **28**, 2724.

[25] W. Querfurth, U. S. P. 1,929,331, Oct. 3, 1933, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1934, **28**, 173.

[26] L. C. Swallen, U. S. P. 1,978,824, Oct. 30, 1934, to Commercial Solvents Corp.; *Chem. Abs.*, 1935, **29**, 177. British P. 437,315, 1935; *Brit. Chem. Abs.* **B**, 1936, 89; *Chem. Abs.*, 1936, **30**, 2202.

[27] M. Ya. Kagan, Russian P. 39,758, 1934; *Chem. Abs.*, 1936, **30**, 3444.

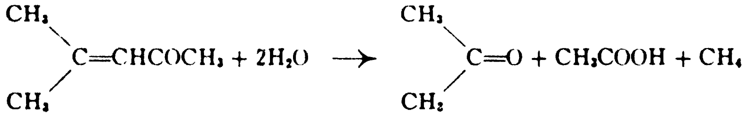
Dreyfus[30] proposes to convert ethanol into acetone by treatment with free oxygen in the vapor phase at temperatures of 350-550°C. A promoter composed of iron oxide and calcium carbonate is employed. Other contact agents include calcium oxide or calcium silicate.[31]

Acetaldehyde vapor at a partial pressure of 25-300 mm. of mercury may be converted into acetone by passage at 400-500°C. over catalysts consisting of zinc, iron, copper and manganese.[32] Esters of aliphatic acids and monohydric alcohols, such as ethyl acetate, are reported to be converted into ketones by treatment at 400-600°C. in the presence of the oxides of iron, manganese or zinc, or the carbonates of calcium, strontium, barium and magnesium.[33]

Also gaseous acetic acid is stated to be converted to acetone by conducting the vapor at 300° to 400°C. over activated carbon admixed with an oxide of calcium or zinc.[34] The mechanism of this reaction when calcium hydroxide is employed has been discussed by Nieuwland.[35] He points out that with the acid in the gaseous phase, the conversion may be described as:

$$\begin{aligned} 2CH_3COOH + Ca(OH)_2 &\longrightarrow (CH_3COO)_2Ca + 2HOH \\ (CH_3COO)_2Ca &\longrightarrow CH_3COCH_3 + CaCO_3 \\ CaCO_3 &\longrightarrow CaO + CO_2 \\ CaO + HOH &\longrightarrow Ca(OH)_2 \end{aligned}$$

Acetone may be prepared by the interaction of acetylene and water as described in Chapter 28. It is interesting to note that mesityl oxide and acetylphthalimide have been recommended for the production of acetone. The activity of various promoters for the hydrolysis of mesityl oxide has been studied.[36] It is stated that the hydrolysis, which may be represented as:



$$(CH_3)_2C{=}CHCOCH_3 + 2H_2O \longrightarrow \begin{matrix} CH_3 \\ CH_2 \end{matrix}{>}C{=}O + CH_3COOH + CH_4$$

may be effected by conducting the vapors of the oxide together with steam, over silica gel. By employing temperatures of 200 to 350°C. at 1 atmosphere pressure, a yield of 19 to 32 per cent of the theoretical amount of acetone is reported. Substitution of aluminum oxide and of thorium oxide for the silica gel is stated to lower the amount of ketone to 8 per cent and 2.3 per cent, respectively.

Acetylphthalimide, $C_6H_5(CO)_2NCOCH_3$, may be subjected to pyrolysis to furnish acetone.[37] Fifty parts of the former substance when heated to 240-325°C. for a period of 2 hours yielded only 1 part of acetone, however.

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[28] G. Bloomfield, L. C. Swallen and F. M. Crawford, U. S. P. 1,945,131, Jan. 30, 1934, to Commercial Solvents Corp.; *Chem. Abs.*, 1934, **28**, 2371; *Brit. Chem. Abs.* **B**, 1934, 953.

[29] G. Bloomfield, L. C. Swallen and F. M. Crawford, U. S. P. 1,978,619, Oct. 30, 1934, to Commercial Solvents Corp.; *Chem. Abs.*, 1935, **29**, 180.

[30] H. Dreyfus, U. S. P. 2,010,066, Aug. 6, 1935; *Chem. Abs.*, 1935, **29**, 6246.

[31] H. Dreyfus, U. S. P. 1,925,311, Sept. 5, 1933; *Chem. Abs.*, 1933, **27**, 5337.

[32] L. C. Swallen, U. S. P. 1,970,782, Aug. 21, 1934, to Commercial Solvents Corp.; *Chem. Abs.*, 1934, **28**, 6160; *Brit. Chem. Abs.* **B**, 1935, 716.

[33] K. Roka, U. S. P. 1,926,632, Sept. 12, 1933, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1933, **27**, 5753.

[34] H. Walter, German P. 627,195, 1936, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1936, **30**, 4180.

[35] J. A. Nieuwland, *Ind. Eng. Chem.*, 1935, **27**, 850; *J. Inst. Pet. Tech.*, 1935, **21**, 371A; *Chem. Abs.*, 1935, **29**, 4981.

[36] A. Zangirolami, *Ann. chim. applicata*, 1934, **24**, 347; *Chem. Abs.*, 1934, **28**, 7245; *Brit. Chem. Abs.* **A**, 1934, 1204.

[37] C. D. Hurd, M. F. Dull and J. W. Williams, *J.A.C.S.*, 1935, **57**, 774; *Brit. Chem. Abs.* **A**, 1935, 748; *Chem. Abs.*, 1935, **29**, 3667.

PROPERTIES AND REACTIONS OF ACETONE

Acetone is a colorless mobile liquid having the following physical constants: b.p. 56.15°C.; m.p. —94.9°C.; d_4^{15} 0.79705; critical temperature 234.4°C.; latent heat of vaporization 125.28 Cal. per kg. at 56.3°C.[38]

In comparing the toxicity of acetone with that of methanol, it has been stated that acetone depresses the heart to a greater extent than does the alcohol, but that recovery is much more complete with the former.[39] With mortality as a criterion, methanol is said to be more toxic. With mixtures of the two, the action of acetone is reported to predominate at high concentrations and that of methanol in low concentrations.

Determination of Acetone. Various methods have been suggested for the qualitative and quantitative determination of acetone. Kolthoff[40] points out that as little as 1 mg. of acetone in a liter of solution can be detected by heating 10 cc. of the solution with 1 g. of solid potassium hydroxide and 10 drops of salicylaldehyde to 70°C. on a water bath. Formation of a red ring on the surface of the solution indicates the presence of acetone. Further, vanillin (*m*-methoxy-*p*-hydroxybenzaldehyde) is said to be as sensitive as salicylaldehyde and to have the added advantage of being a specific reagent for acetone in that it does not react with methyl ethyl or aromatic ketones. A spot test to detect as little as 0.5 mg. of acetone has been advocated.[41] A drop of the solution under analysis is dissolved in ether together with a drop of *o*-nitrobenzaldehyde and the solution evaporated. Chloroform is incorporated in the reaction tube, and if acetone is present, indigotin (indigo blue) is formed.

The quantitative determination of acetone has been accomplished by a number of methods. In one of these the acetone is dissolved in water, and a measured amount of caustic soda and iodine incorporated in the solution. The latter is then acidified with sulphuric acid and the excess iodine titrated with sodium thiosulphate.[42] The method depends upon the oxidation of acetone to sodium acetate and iodoform by caustic soda and iodine. Iodine which has not reacted is estimated after the sodium hydroxide has been neutralized. In a modification of the above procedure, it is suggested that the relative insolubility of iodoform in water[43] be made the basis of determination. In this case the volume of precipitated iodoform is compared with the amount obtained from aqueous acetone solutions of known concentration.[44] Another method of estimating acetone is by reaction with hydroxylamine hydrochloride. The interaction may be represented as,

$$CH_3COCH_3 + H_2NOH \cdot HCl \longrightarrow CH_3CNOHCH_3 + HCl + H_2O$$

---

[38] A table showing the specific gravity of acetone-water mixtures of varied concentrations has been reported by W. Young, *J.S.C.I.*, 1933, 52, 449T; *J. Inst. Pet. Tech.*, 1934, 20, 107A; *Brit. Chem. Abs.* A, 1934, 247; *Chem. Abs.*, 1934, 28, 1237.

[39] R. M. Sklianskaya, F. E. Urieva and L. M. Mashbitz, *J. Ind. Hyg. Toxicol.* 1936, 18, 106; *Chem. Abs.*, 1936, 30, 3088.

[40] I. M. Kolthoff, *Pharm. Weekblad.*, 1918, 55, 1021; *Chem. Abs.*, 1918, 12, 2180; *J.C.S.*, 1918, 114 (2), 377.

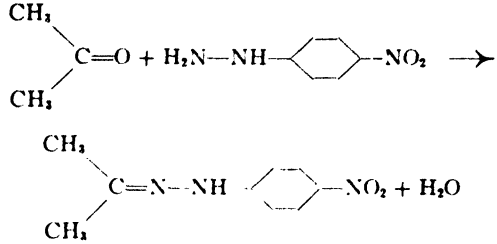
[41] F. Feigl, R. Zappert and S. Vásquez, *Mikrochemie*, 1935, 17, 165; *Brit. Chem. Abs.* A, 1935, 877; *Chem. Abs.*, 1935, 29, 5385.

[42] J. Messinger, *Ber.*, 1888, 21, 3366; *J.S.C.I.*, 1889, 8, 138; *Chem. Zentr.*, 1889, 1, 64. L. F. Goodwin, *J.A.C.S.*, 1920, 42, 39; *Chem. Abs.*, 1920, 14, 1505; *J.S.C.I.*, 1920, 39, 280A. L. M. Christensen and E. I. Fulmer, *Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 180; *Brit. Chem. Abs.* B, 1935, 617. S. D. Sunawala and M. C. T. Katti, *J. Indian Inst. Sci.*, 1935, 18A, 115; *Chem. Abs.*, 1936, 30, 1693; *Brit. Chem. Abs.* B, 1936, 137. See also E. S. Pemberton, S. T. Card and E. C. Craven, *J.S.C.I.*, 1935, 54, 163T; *Chem. Abs.*, 1935, 29, 5812; *Brit. Chem. Abs.* B, 1935, 714. M. S. Platonov and V. A. Plakidina, *J. Gen. Chem. (U.S.S.R.)*, 1934, 4, 472; *Chem. Abs.*, 1935, 29, 2478; *Brit. Chem. Abs.* A, 1934, 1375. A. Lindenberg, *Compt. rend soc. biol.*, 1933, 114, 15; 1936, 122, 317; *Chem. Abs.*, 1934, 28, 75; 1936, 30, 5906; *Brit. Chem. Abs.* A, 1936, 967.

[43] Iodoform is soluble in water to the extent of 0.01 g. per 100 cc. at 25°C.

[44] S. Cornet-Cals and M. R. Cornet-Cals, *Halle aux cuirs*, 1936, 30; *Chem. Abs.*, 1936, 30, 2881.

whereby acetoxime and hydrochloric acid are formed. The amount of acid liberated is then determined by titration with caustic potash.[45] The error which may be introduced by the presence of organic acids is said to be decreased by the use of bromophenol-blue as an indicator. The latter has a yellow color when the *p*H is less than 3.0 and changes to violet in the *p*H range of 3.0 to 3.6. The interaction of acetone with 2,4-dinitrophenylhydrazine to form a precipitate of acetone-2,4-dinitrophenylhydrazone has been advocated for the estimation of the ketone.[46]



Comparison of the weights of dinitrophenylhydrazine employed and of hydrazone obtained forms a basis for estimating the amount of acetone reacting. Also, a quantitative colorimetric estimation of acetone has been reported.[47] The ketone mixture is diluted with water and *o*-nitrobenzaldehyde and caustic soda added. The solution is allowed to stand in the dark for 15 minutes and then compared colorimetrically with known acetone solutions which have been similarly treated.

Decomposition of Acetone. The thermal decomposition of acetone leads primarily to the formation of ketene and methane.

$$CH_3COCH_3 \longrightarrow CH_4 + CH_2{=}CO$$

There is some evidence to show that the breakdown proceeds through a chain mechanism. It has been pointed out that the decomposition may occur by rupture of a molecule of acetone:[48]

$$CH_3COCH_3 \longrightarrow CH_3 + CH_3CO$$

which would be followed by a chain reaction:

$$\begin{aligned} CH_3COCH_3 + CH_3 &\longrightarrow CH_4 + CH_3COCH_2 \\ CH_3COCH_2 &\longrightarrow CH_2{=}CO + CH_3 \end{aligned}$$

In order to ascertain whether the addition of methyl groups brings about a chain reaction in vaporized acetone, the latter was heated with 1 per cent of dimethyl mercury to 350-400°C. Under these conditions the latter decomposed to mercury and methyl radicals. No ketene was produced, indicating that the chain reaction mentioned above had not taken place. Instead, a substance identified as acetonylacetone, $CH_3COCH_2CH_2COCH_3$, was formed in amounts corresponding to the amount of dimethyl mercury incorporated in the reaction zone. It was concluded that the chain reaction given above does not occur below 400°C., but that the acetonyl groups combine among themselves.

$$\begin{aligned} CH_3COCH_3 + CH_3 &\longrightarrow CH_4 + CH_3COCH_2 \\ 2CH_3COCH_2 &\longrightarrow CH_3COCH_2CH_2COCH_3 \end{aligned}$$

---

[45] L. Palfray and S. Tallard, *Compt. rend.*, 1934, **199**, 296; *Brit. Chem. Abs.* **A**, 1934, 992; *Chem. Abs.*, 1935, **29**, 2478.

[46] O. L. Brady and G. V. Elsmie, *Analyst*, 1926, **51**, 77; *Chem. Abs.*, 1926, **20**, 1774; *Brit. Chem. Abs.* **A**, 1926, 394. R. E. Houghton, *Am. J. Pharm.*, 1934, **106**, 62; *Chem. Abs.*, 1934, **28**, 2641; *Brit. Chem. Abs.* **A**, 1934, 425. G. W. Perkins and M. W. Edwards, *Am. J. Pharm.*, 1935, **107**, 208; *Brit. Chem. Abs.* **A**, 1935, 998; *Chem. Abs.*, 1935, **29**, 6166.

[47] C. E. Prélat, *Anales asoc. quim. Argentina*, 1934, **22**, 67; *Chem. Abs.*, 1935, **29**, 81; *Brit. Chem. Abs.* **A**, 1934, 1239.

[48] F. O. Rice, E. L. Rodowskas and W. R. Lewis, *J.A.C.S.*, 1934, **56**, 2497; *Chem. Abs.*, 1935, **29**, 727; *Brit. Chem. Abs.* **A**, 1935, 67.

Also, Allen[49] advocates picturing the decomposition as a chain mechanism. Velocities of reaction at temperatures in the range 462-529°C. were determined by measuring the change in pressure at definite intervals. The breakdown of acetone to ketene and methane was found to proceed smoothly at 529°C. At lower temperatures (462°C.) it was noted that the measured initial pressure was higher than would be obtained by extrapolation of the pressure-time curve to zero (see Fig. 109). It was concluded that this relatively high pressure represents an induction period. Introduction of glass packing into the reaction vessel (a 1-liter flask) was said to affect the reaction in three ways: (1) the shape of the rate-pressure curve, determined by plotting the logarithm of the pressure against that of the reaction rate constant, was changed from a convex to a concave curve; (2) the apparent rate at high pressures was not affected when the reaction was carried out at 529°C., but decreased to one-half its normal value with the temperature at 465°C.; (3) the induction period was no longer apparent at any temperature. These effects were considered proof of a chain mechanism, for, on the chain hypothesis, a short induction period appears naturally as the time necessary for the chain-carrying radicals to attain a steady concentration. Packing is supposed to shorten the chains, thus rendering the induction period inappreciable and reducing the rate most at lower temperatures, where the chains are longest. Further it was suggested that the change of shape of the rate-pressure curve by packing shows the great complexity of the reaction. The mechanism considered most plausible is:

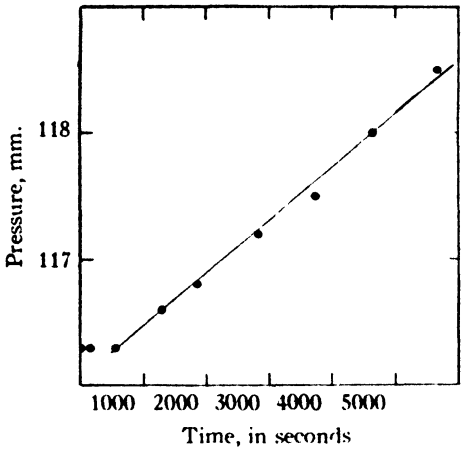


Fig. 109.
Time-Pressure Curve in Thermal Decomposition of Acetone at 462°C. (A. O. Allen)

Courtesy Journal of American Chemical Society

$$\begin{aligned} CH_3COCH_3 &\longrightarrow 2CH_3 + CO \\ CH_3 + CH_3COCH_3 &\longrightarrow CH_4 + CH_2COCH_3 \\ CH_2COCH_3 &\longrightarrow CH_3 + CH_2CO \\ 2CH_3 &\longrightarrow C_2H_6 \\ CH_3 + CH_2COCH_3 &\longrightarrow C_2H_5COCH_3 \end{aligned}$$

It was pointed out that the combination of two acetonyl groups, mentioned before, was not included because the biacetonyl formed would decompose at the temperatures employed.

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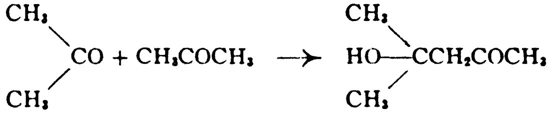
[49] A. O. Allen, *J.A.C.S.*, 1936, **58**, 1052; *Chem. Abs.*, 1936, **30**, 5181; *Brit. Chem. Abs.* **A**, 1936, 939. See also, J. R. Huffmann, *J.A.C.S.*, 1936, **58**, 1815; *Chem. Abs.*, 1936, **30**, 7430; *Brit. Chem. Abs.* **A**, 1936, 1344.

Patat and Sachsse[50] state that although the decomposition of acetone does proceed by free radicals, too few are present to account for the total decomposition. On the other hand, Winkler and Hinshelwood[51] consider that the reaction is homogeneous and that chains must be either absent or very short.

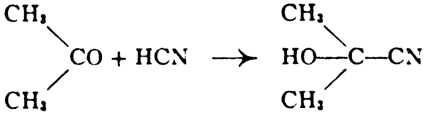
Diacetone Alcohol. When subjected to the action of alkalies, acetone undergoes a condensation similar to the aldol condensation of aldehydes, which results in the formation of diacetone alcohol.



Among the substances aiding in the condensation are sodium, potassium and barium hydroxides, as well as magnesium amalgam.[52] Guinot[53] employs alcohol as a solvent for the alkaline condensing agent. For example, 800 cc. of an alcoholic solution of potassium hydroxide containing 40 g. of the latter was incorporated in 500 g. of ketone at 10°C. The mixture was allowed to stand for 5 hours, neutralized, and distilled to recover diacetone alcohol. It was said that 14 per cent of the acetone was transformed to the alcohol in this manner. For continuous production of diacetone alcohol, acetone may be conducted over solid sodium or potassium hydroxide at 20°C.[54] To separate diacetone alcohol from unchanged acetone, distillation may be carried out at atmospheric pressure after water is added up to 10 per cent of the volume of alcohol present in order to minimize decomposition. When a still temperature of 105-107°C. is reached, practically all of the acetone and some water have been distilled off. The remaining water is removed by vacuum distillation below 105°C. The alcohol may then be distilled off at 166°C. and 760 mm.[55]

Diacetone alcohol has been suggested as a solvent,[56] but it must be employed under neutral or slightly alkaline conditions. In the presence of acids the alcohol tends to decompose to mesityl oxide, which is discussed later in this chapter.

Cyanohydrins. Acetone reacts with hydrogen cyanide to yield an addition product, acetone cyanohydrin.



Scorah and Wilson[57] point out that the addition may be carried out in the liquid phase and at the boiling point of the ketone (56.15°C.). For example, 1 mole of hydrocyanic acid is incorporated in a boiling solution of 1 mole of acetone containing 0.5 per cent of piperidine. After heating is continued for 0.5-1 hour, the products are cooled to 20°C. and acidified with 50 per cent sulphuric acid. Acetone cyanohydrin may then be distilled from the reaction chamber. Addition of quinoline and phosphorus pentoxide is said to bring about a splitting off of a molecule of water from the cyanohydrin, resulting in methacrylonitrile, $CH_2{=}CCNCH_3$. In the preparation of aliphatic cyanohydrins the presence of 0.1 per cent of sodium cyanide is said to accelerate the reaction.[58] One proposed use for acetone cyanohydrin is in the preparation of esters of α-hydroxy fatty acids.[59] For example, 799 g. of the cyanohydrin are heated to 75°C. and 1200 g. of 98 per cent sulphuric acid incorporated. Methanol (100 g.) and hydroquinone (1 g.) are added and the mixture heated on a water bath to 100°C. After 16 hours 300 g. of sodium sulphate are introduced into the reaction flask and the products distilled off. Yields of 545 g. of methyl-α-hydroxy isobutyrate and 218 g. of methyl methacrylate are reported from this procedure.

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[50] F. Patat and H. Sachsse, *Z. physik. Chem.*, 1935, **B31**, 105; *Chem. Abs.*, 1936, **30**, 2471. *Z. Elektrochem.*, 1935, **41**, 493; *Brit. Chem. Abs.* **A**, 1935, 1206; *Chem. Abs.*, 1935, **29**, 7134.

[51] C. A. Winkler and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, 1935, **A149**, 340; *Chem. Abs.*, 1935, **29**, 4246; *Brit. Chem. Abs.* **A**, 1935, 827.

[52] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

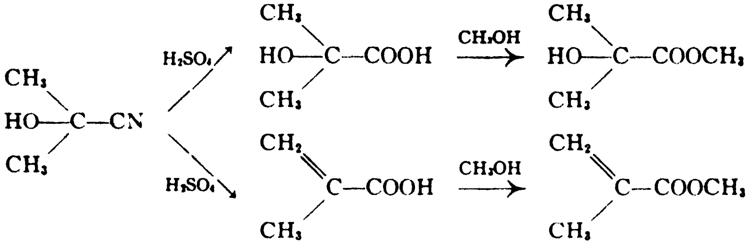
[53] H. Guinot, U. S. P. 1,937,272, Nov. 28, 1933, to Usines de Melle; *Chem. Abs.*, 1934, **28**, 1048.

[54] R. Leopold and B. Schacke, German P. 591,316, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 2371.

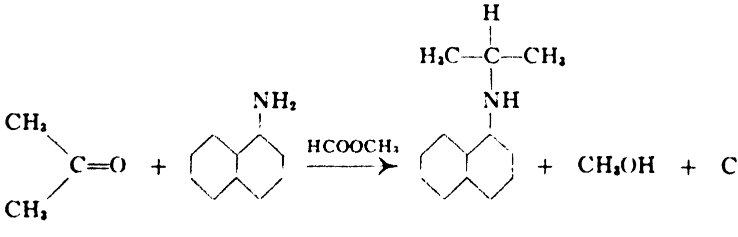
[55] E. E. Connolly, British P. 402,788, 1933, to British Industrial Solvents Ltd.; *Chem. Abs.*, 1934, **28**, 2724; *Brit. Chem. Abs.* **B**, 1934, 266. German P. 608,098, 1935, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1935, **29**, 2550. For a study of the equilibrium and free energy changes in the system acetone-diacetone alcohol, see G. L. Davis and G. H. Burrows, *J.A.C.S.*, 1936, **58**, 311; *Brit. Chem. Abs.* **A**, 1936, 428.

[56] Carleton Ellis, U. S. P. 1,984,061, Dec. 11, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1935, **29**, 948; *Brit. Chem. Abs.* **B**, 1935, 1152. See Chapter 17.

[57] L. V. D. Scorah and J. Wilson, British P. 416,007, 1934, to The Triplex Safety Glass Co.; *Chem. Abs.*, 1935, **29**, 814; *Brit. Chem. Abs.* **B**, 1934, 1003. J. Wilson, British P. 452,285, 1936; *Chem. Abs.*, 1937, **31**, 417; *Brit. Chem. Abs.* **B**, 1936, 1082. See also R. F. B. Cox and R. T. Stormant, *Org. Syntheses*, XV, 1, *John Wiley & Sons, Inc.*, **1935**; *Chem. Abs.*, 1935, **29**, 5070, *Brit. Chem. Abs.* **A**, 1936, 591.



Amines. Acetone reacts with ammonia and with primary and secondary amines to form, respectively, primary, secondary and tertiary amines. For example, acetone may be treated with hydrogen and ammonia at 300°C. and under 200 atmospheres pressure to yield a mixture of isopropylamine and diisopropyl amine, the ratio of the primary to secondary amine being 9:1. An alloy of nickel, sulphur and tungsten is suggested as a contact agent.[60] With a primary amine and acetone in the presence of methyl formate, the production of a secondary amine may be represented as:



It is reported that the above reactants heated to 210°C. for a period of 2 hours give the yield of 90 per cent of the theoretical amount of N-isopropyl-α-naphthylamine.[61] The latter may be further condensed at 240°C. with an aromatic amine to yield a product reported to act as an oxidation inhibitor for rubber.[62] Analogously, acetone interacts with a secondary amine to furnish a tertiary amine. Meuser[63] points out that acetone may be reacted with N-phenyl-β-naphthylamine to furnish N,N-isopropyl phenyl-β-naphthylamine. The reactants are heated in an autoclave to 250°C. with reduced iodides of iron and tin.

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[58] A. D. Macallum, U. S. P. 1,984,415, Dec. 18, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 814; *Brit. Chem. Abs.* B, 1935, 1130. British P. 439,054, 1935; *Chem. Abs.*, 1936, **30**, 2992.

[59] J. W. C. Crawford, British P. 419,457, 1934, to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* B, 1935, 92; *Chem. Abs.*, 1935, **29**, 2547. U. S. P. 2,056,711, Oct. 6, 1936; *Chem. Abs.*, 1936, **30**, 8247. U. S. P. 1,993,089, March 5, 1935; *Chem. Abs.*, 1935, **29**, 2547. U. S. P. 2,041,820, May 26, 1936; *Chem. Abs.*, 1936, **30**, 4871. U. S. P. 2,042,458, June 2, 1936; *Chem. Abs.*, 1936, **30**, 4871. British P. 405,699, 1934; *Chem. Abs.*, 1934, **28**, 4745; *Brit. Chem. Abs.* B, 1934, 313. British P. 427,810, 1935; *Chem. Abs.*, 1935, **29**, 5857; *Brit. Chem. Abs.* B, 1935, 620. British P. 410,208, 1934; *Chem. Abs.*, 1934, **28**, 6157; *Brit. Chem. Abs.* B, 1934, 710. British P. 437,197, 1935; *Chem. Abs.*, 1936, **30**, 2207; *Brit. Chem. Abs.* B, 1936, 11. See also, Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[60] British P. 436,214, 1936, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1936, 55.

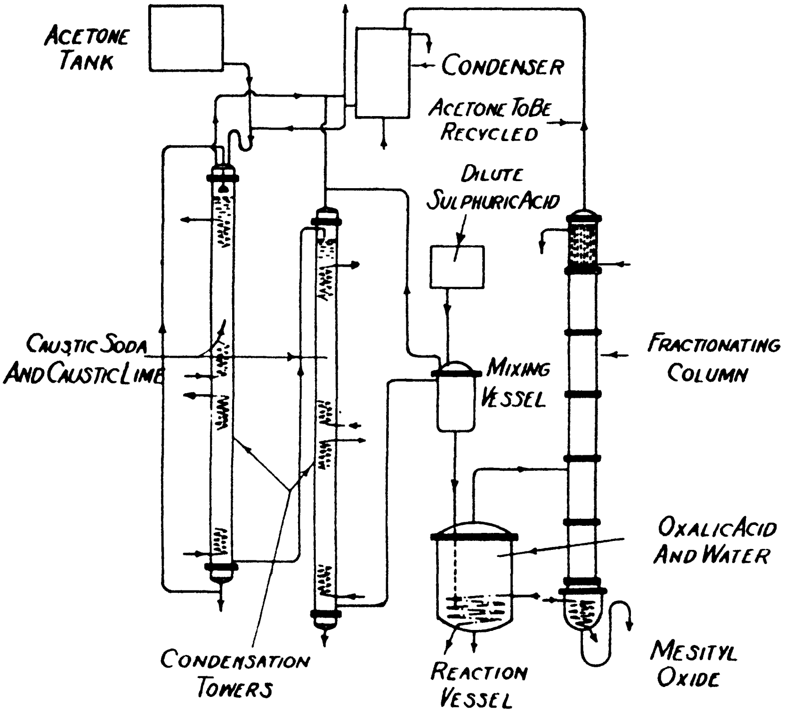
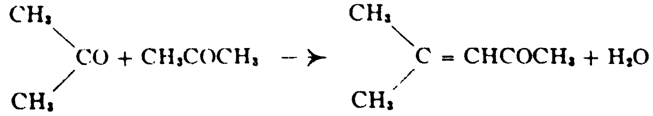


FIG. 110.—Schematic Diagram of Method of Making Mesityl Oxide from Acetone. (O. Fuchs)

Mesityl Oxide. This unsaturated ketone may be prepared from acetone by the action of such agents as anhydrous alkalies, e.g., calcium oxide, or by zinc or hydrogen chloride.[64] In one procedure acetone is treated at 10°C. with an anhy-



$$(CH_3)_2CO + CH_3COCH_3 \longrightarrow (CH_3)_2C = CHCOCH_3 + H_2O$$

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[61] British P. 428,092, 1935, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1935, 665; *Chem. Abs.*, 1935, **29**, 6903. German P. 618,032, 1935; *Chem. Abs.*, 1936, **30**, 107. French P. 776,613, 1935; *Chem. Abs.*, 1935, **29**, 3687.

[62] W. L. Semon, U. S. P. 2,015,696, Oct. 1, 1935, to B. F. Goodrich Co., *Brit. Chem. Abs.* **B**, 1936, 1082; *Chem. Abs.*, 1935, **29**, 8405.

[63] L. Meuser, U. S. P. 1,975,167, Oct. 2, 1935, to Naugatuck Chemical Co.; *Chem. Abs.*, 1934, **28**, 7262; *Brit. Chem. Abs.* **B**, 1935, 841. L. Meuser and P. J. Leaper, British P. 401,353, 1933; *Brit. Chem. Abs.* **B**, 1934, 137; *Chem. Abs.*, 1934, **28**, 2571.

[64] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

drous alkali similar to the ones just mentioned to effect a partial conversion of the ketone to diacetone alcohol.[65] Dilute sulphuric acid is then added in a quantity just sufficient to neutralize the alkali present. The alcohol is admixed with oxalic acid and water at 120°C. to split off the elements of water from the alcohol, producing mesityl oxide in a reported yield of 95 per cent, based on the amount of acetone employed. Unreacted acetone may be distilled from the reaction zone at 56°C. and 760 mm. and recycled (see Fig. 110). The mesityl oxide comes over at 128-130°C. under the same pressure.

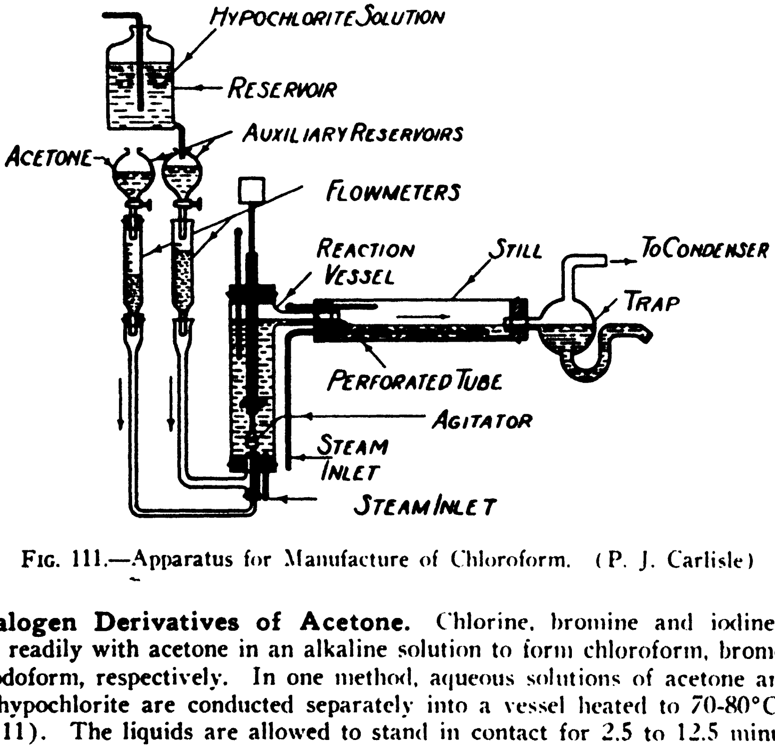
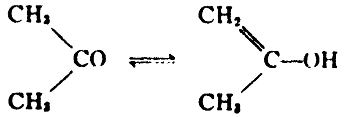


FIG. 111.—Apparatus for Manufacture of Chloroform. (P. J. Carlisle)

Halogen Derivatives of Acetone. Chlorine, bromine and iodine react rather readily with acetone in an alkaline solution to form chloroform, bromoform, and iodoform, respectively. In one method, aqueous solutions of acetone and calcium hypochlorite are conducted separately into a vessel heated to 70-80°C. (see Fig. 111). The liquids are allowed to stand in contact for 2.5 to 12.5 minutes to give a yield of 84-88 per cent of the theoretical amount of chloroform.[66] A di-substituted ketone, *asym*-dichloroacetone is reported to be secured when the halogenation is effected at the boiling point of the ketone.[67] In one case, 1500 g. of acetone were subjected to the action of chlorine at 56°C. to furnish 1612 g. of *asym*-dichloroacetone. It has been noted that the bromination of acetone is retarded by water, and, to a somewhat lesser extent, by alcohols.[68] As a possible explanation, it was suggested that acetone exists in two tautomeric forms,



$$(CH_3)_2CO \rightleftharpoons CH_2{=}C(OH)CH_3$$

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[65] O. Fuchs, U. S. P. 1,925,317, Sept. 5, 1933, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1933, 27, 5337. German P. 630,507, 1936; *Chem. Abs.*, 1937, 31, 117.

[66] P. J. Carlisle, U. S. P. 1,915,354, June 27, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1934, 136; *Chem. Abs.*, 1933, 27, 4252.

[67] W. O. Herrmann and E. Baum, U. S. P. 1,916,979, July 4, 1933, to Consortium für elektrochemische Industrie, G.m.b.H.; *Brit. Chem. Abs.* B, 1934, 393; *Chem. Abs.*, 1933, 27, 4546.

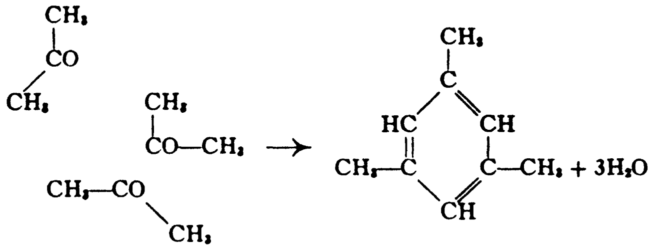
[68] T. Tomonari, *Z. physik. Chem.*, 1936, **B32**, 222; *Brit. Chem. Abs.* A, 1936, 825.

ketonic and enolic, the latter being more reactive with halogens. The retarding effect, therefore, was said to be caused by the formation of a complex addition product of water or alcohol with the ketone form.

Although direct substitution of fluorine in acetone has not been reported, a monosubstituted derivative has been prepared.[69] Bromoacetone is dissolved in ether and heated to 85-95°C. Anhydrous tellurium fluoride is then incorporated in the reaction chamber. The method is said to give 66 per cent of the theoretical yield of fluoroacetone, boiling at 72.5°C.

Miscellaneous Reactions of Acetone. Among the substances which have been obtained from acetone are included mesitylene, isopropyl alcohol, organic acids and peroxides, and keto-alcohols and aldehydes in addition to the compounds previously mentioned.

In the presence of hydrochloric acid, three molecules of acetone unite to form a cyclic compound, mesitylene, 1,3,5-trimethylbenzene.[70] It has been reported that



the amount of mesitylene furnished by this condensation at 175°C. and 100 atmospheres pressure varies with the concentration of the hydrochloric acid.[71] The yield was found to rise rapidly with increasing concentration of hydrochloric acid ($d_4^{20} = 1.19$) until 5 per cent by volume is reached. With proportions of acid between 5 and 50 per cent, a gradual fall in the amount of the cyclic compound occurs, and terpene-like products with a high degree of condensation appear. With a constant concentration of acid at 5 per cent by volume and with varying temperature, the graphical relationship of temperature to yield of mesitylene (based on unrecovered acetone) showed a sharp inflection at 140°C. (see Fig. 112). A similar break was noted at 170°C. when the yield was calculated from the amount of acetone charged into the apparatus. Between 175 and 190°C. the two curves coincided, pointing to a complete utilization of the acetone. At 140°C. 50 per cent of the acetone remains unaffected. At 175-180°C. practically all of the ketone is used up, giving 36 per cent of the cyclic compound.

In another procedure, aluminum oxide is used as a contact agent in place of hydrochloric acid.[72] The oxide, which may be secured by heating a natural alumina hydrate such as bauxite for a period of 1 hour at 600-900°C., is added to acetone, and the two are heated to 330-370°C. under 150-250 atmospheres pressure to give a 40 per cent yield of mesitylene.

The addition of hydrogen to acetone leads to isopropanol. This process is the reverse of the dehydrogenation of isopropanol which was discussed in connection with the preparation of acetone. Acetone and hydrogen may be conducted together over nickel, copper or the oxide or chromite of zinc at temperatures ranging between 40 and 300°C. and at pressures from 1 to 300 atmospheres.[73] In order to suppress any dehydration which may occur with zinc chromite, Lazier[74] proposes to incorporate potassium carbonate in the contact agent. A 10 per cent yield of isopropyl alcohol was obtained as follows. A mixture of 100 cc. of zinc chromite containing 10 per cent of potassium carbonate is placed in a copper reaction tube. Acetone is then pumped at the rate of 1.5 liters per hour through a vaporizing tube heated to 60°C. As the vapors leave the latter they are mixed with compressed hydrogen and conducted over the catalyst bed, which is maintained at 375°C. and a pressure of 200 atmospheres.

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[69] P. C. Ray, H. C. Goswami and A. C. Ray, *J. Indian Chem. Soc.*, 1935, **12**, 93; *Chem. Abs.*, 1935, **29**, 4330; *Brit. Chem. Abs.* A, 1935, 733.

[70] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[71] V. N. Ipatieff, B. N. Dolgov and I. Volnov, *Ber.*, 1930, **63**, 3072; *Chem. Abs.*, 1931, **25**, 2124; *Brit. Chem. Abs.* A, 1931, 207. E. Sucharda and H. Kuczynski (*Rocsniki Chem.*, 1934, **14**, 1182; *Brit. Chem. Abs.* A, 1935, 334; *Chem. Abs.*, 1935, **29**, 6214) recommend that pressures of less than 100 atmospheres and temperatures up to 195°C. be employed.

[72] H. Dohse and C. Schuster, U. S. P. 1,977,178, Oct. 16, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1935, 840; *Chem. Abs.*, 1935, **29**, 181. German P. 579,059, 1934; *Chem. Abs.*, 1934, **28**, 5082.

Controlled oxidation of acetone results in the formation of carboxylic acids. Flemming and Speer[75] report that acetone and air at 200°C. and under 25 atmospheres in the presence of 0.1 to 1 per cent of manganese and cobalt acetate yield acetic acid. A mixture of trimethylacetic and acetic acid is reported from the interaction of acetone, steam and carbon monoxide at 300°C. and 350 atmospheres pressure.[76] Activated charcoal and aluminum chloride are suggested as promoters for the reaction. Selenious oxide is said to be an effective agent for partially oxidizing acetone to a keto-aldehyde with the formation of but little acid.[77] Hydrogen peroxide, prepared *in situ* by the hydrolysis of persulphuric acid, has been employed to oxidize acetone to acetone peroxide.[78] For example, a 13 per cent solution of persulphuric acid is hydrolyzed by heating to 100°C. for 1 minute. It is then cooled to —20°C. and acetone incorporated slowly. Stirring is continued for 15 minutes at the latter temperature. Acetone peroxide may then be extracted with benzene.

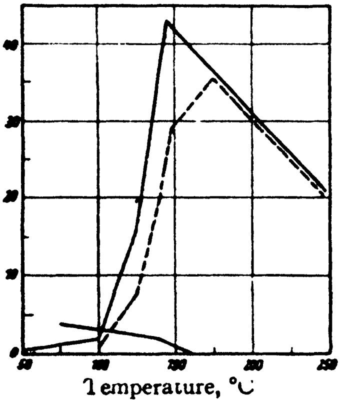

FIG. 112.
Effect of Temperature on Yield of Mesitylene from Acetone. (V. N. Ipatieff, B. N. Dolgov and I. Volnov)

Courtesy Deutsche Chemische Gesellschaft
Courtesy Verlag Chemie G.m.b.H.

Condensation of acetone with a higher ketone leads to the production of keto-alcohols in a manner analogous to the formation of diacetone alcohol. Thus, acetone and ethyl methyl ketone react at 20°C. in the presence of sodium hydroxide to furnish a mixture of 4-hydroxy-4-methyl-2-hexanone and 5-hydroxy-5-methyl-3-hexanone.[79] The latter compounds are suggested as solvents for pyroxylin.

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[73] Carleton Ellis. "Hydrogenation of Organic Substances," Third Edition, D. Van Nostrand Co., Inc., New York, 1930.

[74] W. A. Lazier, U. S. P. 1,895,515, Jan. 31, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1933, 905; *Chem. Abs.*, 1933, 27, 2455.

[75] W. Flemming and W. Speer, U. S. P. 2,005,183, June 18, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 5125.

[76] A. T. Larson, U. S. P. 2,037,654, April 14, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, 30, 3836.

[77] N. N. Mel'nikov, *Uspekhi Khim.*, 1936, 5, 443; *Chem. Abs.*, 1936, 30, 5180.

[78] British P. 444,544, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, 30, 5588; *Brit. Chem. Abs.* B, 1936, 683; *J. Inst. Pet. Tech.*, 1936, 22, 273A.

A number of synthetic resins are prepared by the interaction of acetone, as well as higher ketones, with aldehydes. The condensation products have been proposed for use in molding compositions and as constituents of varnishes.[80]

USES OF ACETONE

Since acetone is one of the best known solvents and because of its ready miscibility with water, alcohol, ether and many esters, mineral and vegetable oils, it finds wide use where solvents are required. Among its miscellaneous applications are the preparation of smokeless powder, storing of acetylene, as a fuel and as a selective solvent for dewaxing lubricating oils.[81]

Acetone has been recommended as a constituent of paint and varnish removers. One such remover contains 20-40 per cent of a petroleum distillate boiling below 115°C., 25-40 per cent of a mixture of methanol, ethanol and acetone, and 20 per cent of ethyl acetate.[82] A composite of 40-60 per cent of a hydrogenated petroleum fraction, 15-40 per cent of acetone and 1-8 per cent of paraffin or ceresin wax has been described as effective for the same purpose.[83] Also, hydrogenated gasoline may be mixed in a volume ratio of 3:7 with isopropanol and acetone. Paraffin wax and cadmium oleate are then incorporated in this solvent to form a liquid effective in removing varnish and lacquer.[84]

In dewaxing lubricating oils, acetone may be employed either alone[85] or mixed with benzol,[86] tetrahydronaphthalene,[87] water-insoluble aliphatic alcohols,[88] higher ketones such as methyl isobutyl or methyl ethyl ketone,[89] *o*-dichlorobenzene,[90] monochlorobenzene,[91] ethylene dichloride,[92] isopropyl ether,[93] bis(2-chloroethyl) ether[94] or a kerosene extract boiling below 300°C.[95] The solvent is added to the oil and the mixture cooled to a point, usually between —10 to —23°C., where the solvent has complete action upon the oil and practically none upon the wax. The precipitated wax is then removed by filtration or centrifuging.

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[79] R. H. Van Schaack, Jr., U. S. P. 1,926,567, Sept. 12, 1933, to Van Schaack Bros. Chemical Works; *Brit. Chem. Abs.* **B**, 1934, 709; *Chem. Abs.*, 1933, **27**, 5751.

[80] Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**.

[81] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. *Cf.* J. N. Crahay, *Ing. chim.*, 1936, **20**, 13; *Chem. Abs.*, 1936, **30**, 7543.

[82] Carleton Ellis, U. S. P. 1,980,043, Nov. 6, 1934, to Chadeloid Chemical Co.; *Brit. Chem. Abs.* **B**, 1935, 960; *Chem. Abs.*, 1935, **29**, 260.

[83] Carleton Ellis, U. S. P. 1,999,165, April 23, 1935, to Chadeloid Chemical Co.; *Chem. Abs.*, 1935, **29**, 4108; *Brit. Chem. Abs.* **B**, 1936, 462.

[84] Carleton Ellis, U. S. P. 2,009,357, July 23, 1935, to Chadeloid Chemical Co.; *Chem. Abs.*, 1935, **29**, 5956; *Brit. Chem. Abs.* **B**, 1936, 752.

[85] R J. Garofalo and C. E. Swift, U. S. P. 1,948,346, Feb. 20, 1934, to Union Oil Co. of Calif.; *Brit. Chem. Abs.* **B**, 1934, 1047; *Chem. Abs.*, 1934, **28**, 2884. B. J. Mair and S. T. Schicktanz, Paper given before Petroleum Division, A.C.S. Meeting, Pittsburgh, Sept. 7, 1936. M. R. Cannon and M. R. Fenske, *Ind. Eng. Chem.*, 1936, **28**, 1035; *Brit. Chem. Abs.* **B**, 1936, 1077; *Chem. Abs.*, 1936, **30**, 7829.

[86] F. X. Govers, U. S. P. 1,945,350, Jan. 30, 1934, to Indian Refining Co.; *Chem. Abs.*, 1934, **28**, 2520; *Brit. Chem. Abs.* **B**, 1934, 919; *J. Inst. Pet. Tech.*, 1934, **20**, 192A. U. S. P. 1,964,985, July 3, 1934; *J. Inst. Pet. Tech.*, 1934, **20**, 539A; *Chem. Abs.*, 1934, **28**, 5224. U. S. P. 2,003,664, June 4, 1935; *Chem. Abs.*, 1935, **29**, 4931; *J. Inst. Pet. Tech.*, 1935, **21**, 312A. Canadian P. 355,522, 1936, to Texaco Development Corp.; *Chem. Abs.*, 1936, **30**, 2748. German P. 600,619, 1934, to Indian Refining Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 541A. G. B. Bryant and F. X. Govers, U. S. P. 1,969,201, Aug. 7, 1934, to Indian Refining Co.; *Chem. Abs.*, 1934, **28**, 6297; *Brit. Chem. Abs.* **B**, 1935, 617. H. H. Gross and J. Opryshek, U. S. P. 2,049,059, Aug. 28, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 457A. W. P. Gee, W. Kiersted and B. Y. McCarty, *Nat. Pet. News*, 1936, **28**, 29; *J. Inst. Pet. Tech.*, 1936, **22**, 358A. M. L. Langworthy, U. S. P. 1,956,036, April 24, 1934, to Texas Co.; *Brit. Chem. Abs.* **B**, 1935, 136; *Chem. Abs.*, 1934, **28**, 4218; *J. Inst. Pet. Tech.*, 1934, **20**, 427A. R. E. Manley, U. S. P. 1,980,071, Nov. 6, 1934, to Texas Co.; *Chem. Abs.*, 1935, **29**, 335; *J. Inst. Pet. Tech.*, 1935, **21**, 66A. V. Voorhees, U. S. P. 1,956,780, May 1, 1934, to Standard Oil Co. of Ind.; *Brit. Chem. Abs.* **B**, 1935, 215; *Chem. Abs.*, 1934, **28**, 4218. W. A. Myers, *Oil and Gas J.*, 1935, **34**, 78; *J. Inst. Pet. Tech.*, 1935, **21**, 259A.

[87] H. van der Waerden, Canadian P. 357,974, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 4662. British P. 430,485, 1935, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1935, **29**, 8319; *Brit. Chem. Abs.* **B**, 1935, 759; *J. Inst. Pet. Tech.*, 1935, **21**, 344A.

[88] H. Svanoe, U. S. P. 1,981,758, Nov. 20, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 983; *Chem. Abs.*, 1935, **29**, 589.

[89] F. X. Govers, Canadian P. 354,130, 1935, to Texaco Development Corp.; *Chem. Abs.*, 1936, **30**, 1553. U. S. P. 2,054,416, Sept. 15, 1936; *Chem. Abs.*, 1936, **30**, 7839; *J. Inst. Pet. Tech.*, 1936, **22**, 549A. H. H. Gross and W. V. Overbaugh, British P. 445,172, 1936, to Texaco Development Corp.; *Chem. Abs.*, 1936, **30**, 6549; *Brit. Chem. Abs.* **B**, 1936, 681; *J. Inst. Pet. Tech.*, 1936,

Also, sulphur may be separated from hydrocarbons by the action of acetone with aluminum or zinc chlorides[96] or caustic soda, or potash.[97] It has been reported that acetone, combined with ammonia, is effective in removing unsaturated constituents from mineral oils.[98] A lubricant said to be free flowing when kept under pressure and away from air, but which assumes a heavy consistency when exposed to the atmosphere, may be secured by admixing an extreme pressure lubricant with acetone, carbon dioxide and rubber cement.[99] The lubricant is recommended for use in chassis bearings. Further, acetone is suggested as a solvent for cellulose acetate,[100] asphalt,[101] and tar.[102] Among the miscellaneous uses for which acetone has been employed are included cleansing agents,[103] a solvent for wood preservers,[104] and as a pickling solution for steel when mixed with sulphuric acid.[105] It is interesting to note that a substituted derivative of acetone, dihydroxyacetone, is reported to be a good antidote for hydrocyanic (prussic) acid poisoning.[106]

KETENE

It has been previously mentioned that the thermal decomposition of acetone leads to the formation of methane and ketene.

$$CH_3COCH_3 \longrightarrow CH_4 + CH_2{=}CO$$

Besides the theoretical aspect of the above decomposition, practical production of ketene has also received some attention. For example, ketene may be obtained by conducting acetone vapors through a reaction chamber composed of chromium

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22, 269A. For use of acetone or methyl ethyl ketone mixed with benzene, toluene, xylene or cumene, see F. X. Govers, U. S. P. 2,060,805 and 2,061,541, Nov. 17, 1936, to Indian Refining Co.; *Chem. Abs.*, 1937, **31**, 849; *J. Inst. Pet. Tech.*, 1937, **23**, 76A.

[90] B. Y. McCarty, U. S. P. 2,024,107, Dec. 10, 1935, to Texas Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 104A.

[91] British P. 413,307, 1934, to Standard Oil Co. of Ind.; *Brit. Chem. Abs.* **B**, 1934, 871; *Chem. Abs.*, 1935, **29**, 594.

[92] French P. 762,949, 1934, to Aktiebolaget Separator-Nobel; *Chem. Abs.*, 1934, **28**, 5224.

[93] E. W. Reid, U. S. P. 1,947,359, Feb. 13, 1934, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1934, **28**, 2515. Canadian P. 356,140, 1936; *Chem. Abs.*, 1936, **30**, 2746.

[94] S. H. Diegs and J. M. Page, U. S. P. 1,976,544, Oct. 9, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1934, **28**, 7518; *J. Inst. Pet. Tech.*, 1935, 21, 27A.

[95] C. M. Kellogg, U. S. P. 2,047,826, Aug. 14, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 456A.

[96] I. Levine, U. S. P. 1,950,735, March 13, 1934, to Universal Oil Products Co.; *Brit. Chem Abs.* **B**, 1935, 215; *Chem. Abs.*, 1934, **28**, 3578.

[97] B. A. Stagner, British P. 425,623, 1935; *Chem. Abs.*, 1935, **29**, 5645; *Brit. Chem. Abs.* **B**, 1935, 441.

[98] W. H. Volck, U. S. P. 2,047,755, July 14, 1936, to Calif. Spray-Chemical Corp.; *J. Inst. Pet. Tech.*, 1936, **22**, 456A; *Chem. Abs.*, 1936, **30**, 6181.

[99] J. F. Werder, U. S. P. 1,995,371, March 26, 1935, one-half to E. Rogers; *Chem. Abs.*, 1935, **29**, 3151.

[100] See, for example, French P. 785,036, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 1559. C. Dreyfus and W. Whitehead, U. S. P. 1,958,238, May 8, 1934, to Celanese Corp. of America; *Brit. Chem. Abs.* **B**, 1935, 223; *Chem. Abs.*, 1935, **29**, 4231. British P. 444,935, 1936, to British Celanese, Ltd.; *Brit. Chem. Abs.* **B**, 1936, 491.

[101] French P. 780,112, 1935, to Alexander Wacker Ges. für elektrochemische Industrie G.m.b.H.; *Chem. Abs.*, 1935, **29**, 6044.

[102] E. O. Rhodes and F. D. Hager, Canadian P. 336,568, 1933, to The American Tar Products Co., Inc.; *Chem. Abs.*, 1934, **28**, 1846.

[103] R. Wille, German P. 616,885, 1935; *Chem. Abs.*, 1936, **30**, 543. U. S. P. 1,993,469, March 5, 1935; *Brit. Chem. Abs.* **B**, 1936, 1070.

[104] C. H. Siever, U. S. P. 1,983,248, Dec. 4, 1934; *Chem. Abs.*, 1935, **29**, 576; *Brit. Chem. Abs.* **B**, 1935, 1041.

[105] O. Fakler, French P. 783,758, 1935; *Chem. Abs.*, 1935, **29**, 7931.

[106] C. Heymans and H. Handovsky, *Compt. rend. soc. biol.*, 1934, 117, 83; *Chem. Abs.*, 1935, **29**, 509.

and iron which is heated to 550°C.[107] The gases issuing from the heating zone are immediately led to a second chamber (made of copper) which is heated to temperatures of 600 to 750°C. (see Fig. 113). In both steps the pressure is held at 5 lbs. per sq. in. Another proposal is to pass acetone vapors directly into a copper tube heated to 700-850°C., the contact time of the vapors being less than 1 second.[107a]

Because of its instability, it has been proposed that ketene be dissolved, as quickly as it is formed, in an inert solvent, when the unsaturated ketone is to be employed in further synthesis. Thus, the gases secured by thermal decomposition of acetone are scrubbed at 35-55°C. (Fig. 114) with acetone and then conducted into another portion of acetone at 0°C.[108] At the lower temperature a solution of ketene in acetone is formed which may then be utilized in various acetylation reactions. Other solvent liquids mentioned are pentane, hexane, benzene, diethyl ether and methyl ethyl ketone. If the ketene is to be used directly the liquid with which it is to react may be substituted for the solvent liquid. Thus, the gaseous decomposition products are introduced directly into acetic acid to form acetic anhydride or into 2-ethoxyethanol to form 2-ethoxyethyl acetate.[109] Wiezevich and Frolich[110] suggest the production of ketene by passing acetone through a column of molten lead contained in a reaction vessel lined with fireclay. The lead is maintained at the required temperature (600-900°C.) by circulation of a portion of it through a heating coil.

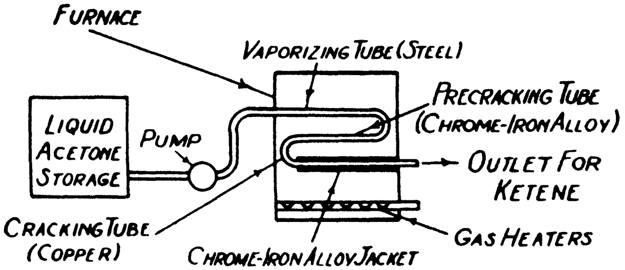

FIG. 113.—Sketch of Method for Thermal Decomposition of Acetone to Ketene. (G. H. Reid)

One method for the laboratory preparation of ketene is as follows.[111] Acetone is dropped directly from a separatory funnel into a quartz reaction tube heated to 650-750°C. The exit gases are led into a Pyrex tube immersed in solid carbon dioxide in order to condense ketene and undecomposed acetone. At the end of a reaction period of 0.5 hour the ketene is distilled off by warming the solution rapidly to the boiling point of acetone (56°C.). The receiver for the distillate is maintained at —80°C. For larger-scale production with the same type of reaction tube, temperatures greater than 750°C. may be employed and unreacted acetone may be recycled through the furnace.[111a] (See Fig. 115.) It is stated that the best yield results when less than 10 per cent of the acetone is decomposed per passage.

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[107] G. H. Reid, Canadian P. 355,617, 1936, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1936, **30**, 2578. British P. 413,709, 1934; *Brit. Chem. Abs.* **B**, 1934, 825; *Chem. Abs.*, 1935, **29**, 482. French P. 749,245, 1933; *Chem. Abs.*, 1933, **27**, 5757.

[107a] G. D. Graves and C. H. Greenewalt, U. S. P. 2,069,243, Feb. 2, 1937, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, **31**, 1826.

[108] G. H. Law, U. S. P. 1,942,110, Jan. 2, 1934, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1934, **28**, 1718. British P. 397,025, 1933; *Chem. Abs.*, 1934, **28**, 780; *Brit. Chem. Abs.* **B**, 1933, 955. Canadian P. 355,618, 1936; *Chem. Abs.*, 1936, **30**, 2578. French P. 750,804, 1933; *Chem. Abs.*, 1934, **28**, 1052.

[109] C. O. Young and G. H. Reid, U. S. P. 1,926,642, Sept. 12, 1933, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1933, **27**, 5753. French P. 730,724, 1932; *Chem. Abs.*, 1933, **27**, 306. Canadian P. 338,162, 1933; *Chem. Abs.*, 1934, **28**, 1718. German P. 604,910, 1934; *Chem. Abs.*, 1935, **29**, 813.

[110] P. J. Wiezevich and P. K. Frolich, British P. 396,568, 1933, to Standard Oil Development Co.; *Chem. Abs.*, 1934, **28**, 483; *Brit. Chem. Abs.* **B**, 1933, 905. French P. 742,985, 1933; *Chem. Abs.*, 1933, **27**, 3722.

[111] F. O. Rice, J. Greenberg, C. E. Waters and R. E. Vollrath, *J.A.C.S.*, 1934, **56**, 1760; *Chem. Abs.*, 1934, **28**, 6104; *Brit. Chem. Abs.* **A**, 1934, 1091.

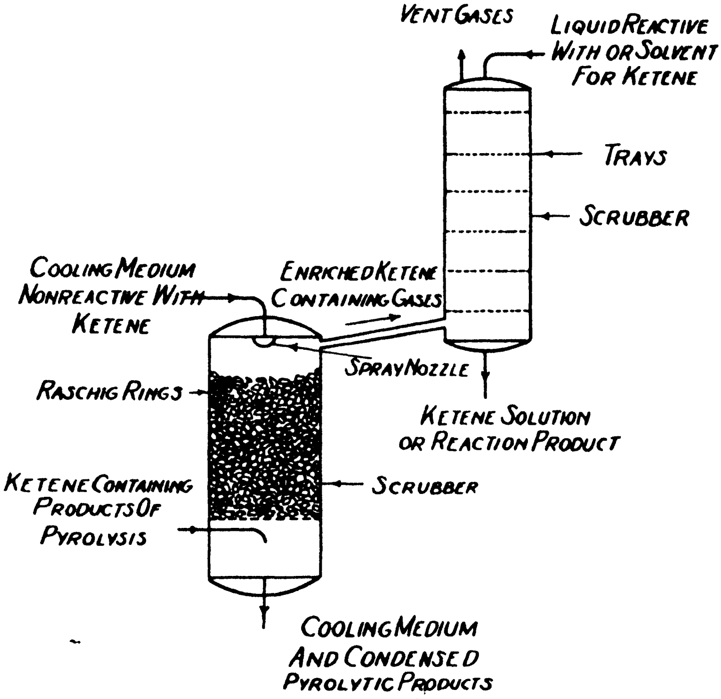
Vent Gases
Liquid Reactive With or Solvent For Ketene
Trays
Scrubber
Cooling Medium Nonreactive With Ketene
Enriched Ketene Containing Gases
Spray Nozzle
Raschig Rings
Ketene Solution or Reaction Product
Ketene Containing Products Of Pyrolysis
Scrubber
Cooling Medium And Condensed Pyrolytic Products

Fig. 114.—Apparatus for Forming Ketene Reaction Products. (G. H. Law)

Also, ketene may be produced from acetic acid or acetic anhydride by thermal treatment.

$$2CH_3COOH \longrightarrow (CH_3CO)_2O + H_2O \longrightarrow 2CH_2{=}CO + H_2O$$

Thus, acetic acid may be heated to 740°C. at 35 mm. pressure in the presence of sodium phosphate, which promotes the formation of the anhydride.[112] In the thermal treatment of acetic anhydride to give ketene, Wiezevich[113] suggested heating the anhydride to 800-1000°C. for 5 seconds by passing through a heated copper vessel and then suddenly cooling the product. Also, there is introduced into the reacted stream an organic liquid insoluble in water and inert to ketene to facilitate the subsequent settling out of water. Recovery of the ketene, unused acid anhydride and added organic liquid is then made. The latter may be chlorobenzene, butyric acid, *sec*-amyl acetate, phenetol or isopropyl ether.

[111a] F. O. Rice, U. S. P. 1,879,497, Sept. 27, 1932, to Röhm and Haas Co.; *Chem. Abs.*, 1933, 27, 313.

[112] French P. 777,483, 1935, to Consortium für elektrochemische Industrie G.m.b.H.; *Chem. Abs.*, 1935, 29, 4029. British P. 435,219, 1935; *Brit. Chem. Abs.* B, 1935, 1085; *Chem. Abs.*, 1936, 30, 1072.

[113] P. J. Wiezevich, U. S. P. 2,045,739, June 30, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, 30, 5597.

Properties and Uses of Ketene. Ketene is a gas at ordinary temperatures; it can be condensed to a liquid boiling at —56°C. and solidifying at —151°C.[114] The substance tends to polymerize to resinous matter at ordinary temperatures, although the pure liquid is stable at —80°C. Polymerization may be inhibited to a considerable extent by various solvents.[115]

The photochemical decomposition of ketene has been studied to determine the mechanism which it follows.[116] One apparatus consisted of a cylindrical quartz cell of 20 cc. capacity immersed in a constant-temperature water bath with a window of crystal quartz. Illumination was secured with a quartz mercury vapor lamp. It was found that the decomposition of ketene is accompanied by a pressure increase and that the gaseous products are carbon monoxide and ethylene. In addition a solid film was deposited gradually on the walls during illumination. When only ketene was present in the illuminated zone the reaction yielded quantitatively carbon monoxide and ethylene in the theoretical ratio. Also, it was noted that the reaction, as measured by the increase in pressure, stops before all the ketene has been consumed. Since the same result occurred when ethylene was added, it was concluded that the retardation of the decomposition was due to the presence of the latter. The solid deposit was assumed to have the composition $(CH_2)_n$, since all of the original ketene was accounted for either as free carbon monoxide or as undecomposed ketene, and because no hydrogen or deposits of free carbon were observed among the products. From these data it was deduced that the primary reaction upon absorption of light is:

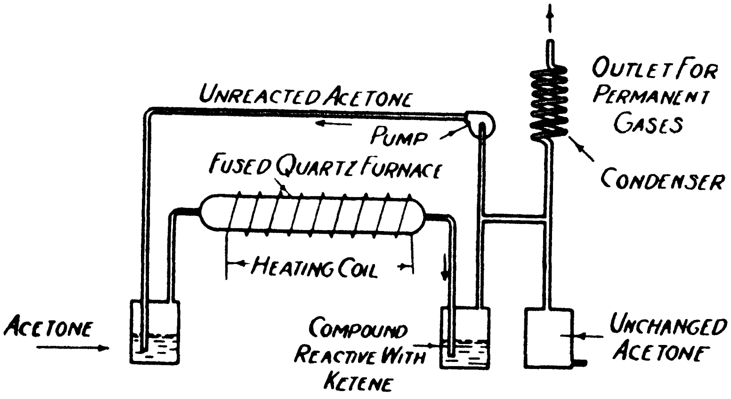

Fig. 115.—Method of Preparation of Ketene, Employing Recycling Operation. (F. O. Rice)

$$H_2C{=}CO \longrightarrow H_2C + CO$$

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[114] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[115] Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[116] W. F. Ross and G. B. Kistiakowsky, *J.A.C.S.*, 1934, 56, 1112; *Chem. Abs.*, 1934, 28, 4314; *Brit. Chem. Abs.* A, 1934, 740.

Further, from the information obtained that the quantum yield with the 3130Å. line was near unity, the conclusion was made that the reaction:

$$H_2C{=}CO + CH_2{=} \longrightarrow CO + C_2H_4$$

does not occur to any significant extent, so that methylene radicals must react with each other to form ethylene. The retardation and finally complete discontinuance of pressure increase was thought to be attributable to the reaction of methylene groups with ethylene, the ultimate product being the solid polymer. On the other hand, Norrish, Crone and Saltmarsh[117] maintain that the reaction between a methylene group and ketene does take place rather than the combination of methylene groups.

Acetylation with Ketene. The addition of ketene to alcohols results in acetylation of the latter.

$$ROH + CH_2{=}CO \longrightarrow ROOCCH_3$$

where *R* is an alkyl, cycloalkyl or aryl group. Ketene is a powerful acetylating agent, and, under proper conditions, will add to most organic substances containing active hydrogen atoms, provided that the compounds can be liquefied or dissolved in a solvent inactive toward ketene.[118] In the procedure, 10 g. of the substance to be acetylated were placed in a reaction flask, fitted with inlet and outlet tubes. The inlet tube was connected with a reservoir containing ketene at —80°C. By allowing this reservoir to warm up, ketene could be passed through the reaction tube at a convenient rate. The outlet from the latter was connected to a third tube, kept at —80°C., in which the unreacted ketene was condensed. The reaction vessel was heated in an oil bath above the melting point of the compound to be acetylated. In this manner cetyl alcohol was converted at 180°C. into cetyl acetate, *ter*-butyl alcohol at 80°C. into *ter*-butyl acetate, and phenol at 183°C. into phenyl acetate. It is interesting to note that attempts to acetylate benzamide by means of ketene at 180°C. resulted in the production of benzonitrile and acetic anhydride. The probable course of this reaction was said to be:

$$\begin{aligned} CH_2{=}CO + C_6H_5CONH_2 &\longrightarrow C_6H_5CONHCOCH_3 \\ C_6H_5CONHCOCH_3 &\longrightarrow C_6H_5CN + CH_3COOH \\ CH_3COOH + CH_2{=}CO &\longrightarrow (CH_3CO)_2O \end{aligned}$$

For the production of phenyl acetate from ketene and phenol 0.5 to 2 per cent of sulphuric acid may be employed as a promoter to give a reported yield of 92-93 per cent of the theoretical amount of phenyl acetate, using a contact period of 1.5 hours.[119]

Hurd and Williams[120] have studied the interaction of ketene with thioalcohols, aromatic aldehydes, hydroxy acids and salicylic acid. With ethanethiol, the acetylation may be represented as:

$$CH_2{=}CO + C_2H_5SH \longrightarrow CH_3COSC_2H_5$$

To effect this transformation, 4 g. of liquid ketene and 3.5 g. of ethanethiol were mixed and kept at —80°C. for 3 days and then warmed to 20°C. On distillation,

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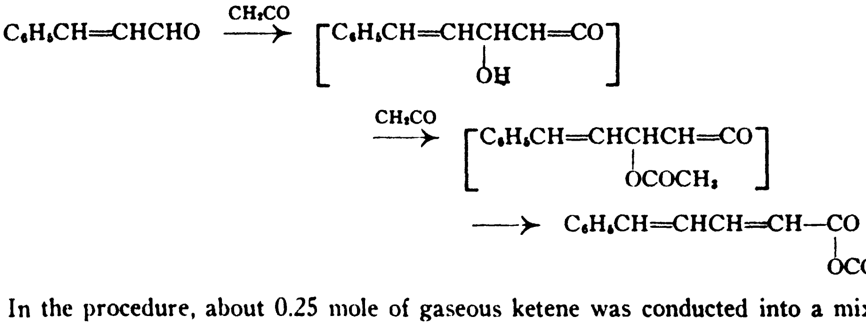
[117] R. G. W. Norrish, H. G. Crone and O. D. Saltmarsh, *J.A.C.S.*, 1934, **56**, 1644; *Brit. Chem. Abs.* **A**, 1934, 976; *Chem. Abs.*, 1934, **28**, 5337.

[118] F. O. Rice, J. Greenberg, C. E. Waters and R. E. Vollrath, *J.A.C.S.*, 1934, **56**, 1760; *Brit. Chem. Abs.* **A**, 1934, 1091; *Chem. Abs.*, 1934, **28**, 6104. For a discussion of the heats of reaction of ketene with alcohols, see F. O. Rice and J. Greenberg, *J.A.C.S.*, 1934, **56**, 2268; *Chem. Abs.*, 1935, **29**, 673; *Brit. Chem. Abs.* **A**, 1935, 36. *Cf.* P. K. Frolich and P. J. Wiezevich, U. S. P. 2,018,759, Oct. 29, 1935, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1936, 1032; *Chem. Abs.*, 1936, **30**, 107.

[119] G. D. Graves, U. S. P. 2,007,968, July 16, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1936, 633; *Chem. Abs.*, 1935, **29**, 5857. British P. 436,885, 1935; *Brit. Chem. Abs.* **B**, 1936, 11.

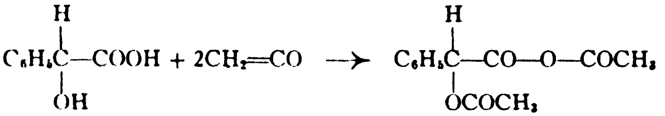
[120] C. D. Hurd and J. W. Williams, *J.A.C.S.*, 1936, **58**, 962; *Chem. Abs.*, 1936, **30**, 5182.

5.1 g. of ethylthioacetate were collected between 109 and 115°C. Cinnamic aldehyde unites with ketene in the presence of fused potassium acetate to form an anhydride of β-styrylacrylic acid.



$$C_6H_5CH{=}CHCHO \xrightarrow{CH_2CO} \left[C_6H_5CH{=}CH\underset{\overset{|}{OH}}{C}HCH{=}CO\right] \xrightarrow{CH_2CO} \left[C_6H_5CH{=}CH\underset{\overset{|}{OCOCH_3}}{C}HCH{=}CO\right] \longrightarrow C_6H_5CH{=}CHCH{=}CH{-}\underset{\overset{|}{OCOCH_3}}{CO}$$

In the procedure, about 0.25 mole of gaseous ketene was conducted into a mixture of 2 g. of fused potassium acetate and 10 g. of cinnamic aldehyde. The products were dissolved in ether and extracted with a 10 per cent caustic soda solution. When sulphuric acid was added to the alkaline extract β-styrylacrylic acid crystallized out. The addition of ketene to mandelic acid results in the formation of an acid anhydride.



$$C_6H_5\underset{\overset{|}{OH}}{\overset{\underset{|}{H}}{C}}{-}COOH + 2CH_2{=}CO \longrightarrow C_6H_5\underset{\overset{|}{OCOCH_3}}{\overset{\underset{|}{H}}{C}}{-}CO{-}O{-}COCH_3$$

To illustrate this, 0.08 mole of ketene gas is passed into a solution of 5 g. (0.033 mole) of mandelic acid in acetone. The acetone is then removed by distillation under reduced pressure, leaving acetylmandelic acetic anhydride, a viscous, light red liquid. Acetylsalicylic acetic anhydride may be secured in a similar manner from salicylic acid (*o*-hydroxybenzoic acid) and ketene. Addition of water to the anhydride furnishes acetylsalicylic acid.

Also, it has been reported that acetylation may proceed through a Friedel-Crafts reaction.[121] Ketene was passed into a suspension of 120 g. of aluminum chloride in 100 cc. of benzene, maintained at 0°C. Stirring was continued until evolution of hydrogen chloride ceased. The product was poured on ice and extracted with benzene and the extract washed with water, dried and distilled. Two cuts were retained: one, boiling at 90°C. under 15 mm. pressure, contained 15 g. of acetophenone ($C_6H_5COCH_3$); the second, which boiled at 110°C. under 15 mm. pressure, consisted of 7 g. of *p*-ethylacetophenone. It was thought probable that the formation of the latter compound was due to the presence of ethylene in the ketene. Acetyl chloride, also an acetylating agent, may be prepared by passing ketene and hydrogen chloride at about 100°C. over active carbon or silica gel.[122]

One of the suggested uses for the acetylating property of ketene is in the preparation of an accelerator for vulcanizing rubber.[123] Ketene is prepared by conducting acetone vapors through a silicon dioxide tube heated to 600-700°C. and equipped with a copper spiral. The gases issuing from the tube are led through a condenser to remove unchanged acetone. The ketene is then passed into a solution of mercaptobenzothiazole, $C_6H_4(NSC{\cdot}SH)$, in chloroform. The acetylated thiazole is a deactivated compound which may be reactivated by heating just before it is to be used in the vulcanization step.

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[121] F. S. Spring and T. Vickerstaff, *J.C.S.*, 1935, 1873; *Brit. Chem. Abs.* A, 1936, 726; *Chem. Abs.*, 1936, **30**, 1750.

[122] W. Eschenbach, German P. 638,441, 1936; *Chem. Abs.*, 1937, **31**, 1042.

[123] D. F. Twiss, D. J. Hadley and F. A. Jones, British P. 420,852, 1934, to Dunlop Rubber Co., Ltd.; *Brit. Chem. Abs.* B, 1935, 163; *Chem. Abs.*, 1935, **29**, 3552.

The reaction of ketene with haloamines has been investigated.[124] Among the latter substances were monochloroamine, dibromoamine, nitrogen trichloride and dimethylchloramine. In the procedure ether solutions of the amine and ketene were cooled to —60°C. and admixed. At the end of 3 hours, the reactants were warmed to room temperature (20°C.) and the precipitate which formed was filtered. Some of the results obtained are indicated in Table 101.

TABLE 101.—*Reaction of Ketene with Haloamines.*

Reactants	Yield, %	M. P., °C.	Formula of Product
$CH_2CO + NH_2Cl$	73	111–112	$CH_3CONHCl$
$CH_2CO + NHBr_2$	18	88–89	$CH_2BrCONH_2$
$CH_2CO + (CH_3)_2NCl$			$CH_2ClCON(CH_3)_2$
$CH_2CO + NCl_3$	14	114–115	$CH_2ClCONH_2$

Polymerization of Ketene. Rice and Greenberg[125] report that ketene does not polymerize to an appreciable extent in the gas phase. When introduced into a Pyrex vessel over mercury the gas showed no decrease in volume over a period of an hour. Brown spots of polymerized ketene then began to appear on the surface of the glass, but the formation of these was erratic. However, liquid

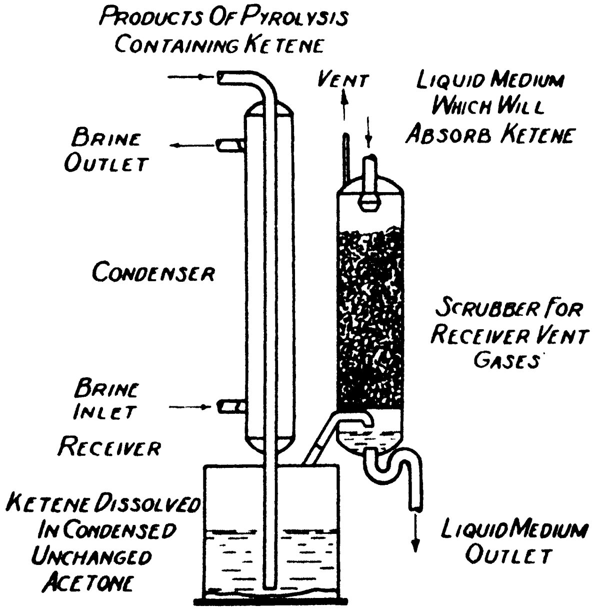

FIG. 116.—Sketch of Apparatus for Preparation of Diketene. (G. H. Law)

ketene was reported to polymerize completely in 1.5 hours, when it was allowed to warm up from —80°C. to 0°C. The rate of polymerization was stated to follow a bimolecular law.[126] Further, it was pointed out that the polymerization is entirely independent of the presence or absence of oxygen, peroxides, hydroquinone and anthraquinone.

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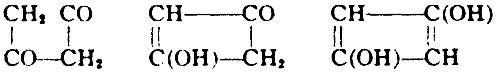
[124] G. H. Coleman, R. L. Peterson and G. E. Goheen, *J.A.C.S.*, 1936, 58, 1874; *Chem. Abs.*, 1936, 30, 8155; *Brit. Chem. Abs.* A, 1936, 1495; *Proc. Iowa Acad. Sci.*, 1935, 42, 122; *Chem. Abs.*, 1936, 30, 8155.

[125] F. O. Rice and J. Greenberg, *J.A.C.S.*, 1934, 56, 2132; *Chem. Abs.*, 1935, 29, 116; *Brit. Chem. Abs.* A, 1935, 1336.

Controlled polymerization of ketene to cyclobutane-1,3-dione, b.p. 127°C., has been carried out with the aid of such metals as steel, copper or chrome nickel steel.[127] For example, ketene is first separated from its acetone solution by cooling to solidify the acetone. Ketene is then liquefied by liquid air, placed in a steel bomb, and allowed to warm up to 25°C. under its own pressure. Cyclobutane-1,3-dione is said to be furnished in amounts up to 85 per cent of theoretical. Also, it has been suggested that the ketene-containing gases from the pyrolysis of acetone be utilized to prepare diketene directly.[128] Such gases may contain, by volume, about 8 per cent of ketene, 10 per cent of methane, 3 per cent of ethylene and carbon monoxide and about 79 per cent of unchanged acetone. The latter is removed by conducting the gases through a brine-cooled condenser (see Fig. 116). The ketene dissolves in the liquid acetone, forming a 10 per cent solution which leaves the condenser at —10°C. and is collected in an uncooled receiver. As the temperature in the receiver rises, the ketene polymerizes slowly to diketene. Uncondensed gases are led to a tower where they are scrubbed with acetone to recover any uncondensed ketene.

Constitution of Diketene. The structure of diketene may be represented as a diketone, keto-enol or dienol.



Measurements of the dipole moment, molecular refractivity and heat of formation have been employed to establish the constitution of this dimer.[129] The dipole moment[130] of dimeric ketene was estimated to be 3.15 at 25°C. in benzene solution and 3.30 in carbon tetrachloride. Calculated values of the dipole moment for the diketone form is zero, for the keto-enol form, 3.0-3.2, and for the dienolic form, 0-3.3. On this basis the keto-enol form was stated to be most probable. Also, measurement of the molecular refractivity[131] substantiated the keto-enol form. In this case the refractivity of dimeric ketene was found to be 20.14, while that calculated for the diketone was 18.99, for the keto-enol, 20.16, and for the dienol, 21.32. The observed heat of formation of diketene (1081 Cal. per mole) was found to be compatible with those calculated for the diketone form (1101 Cal. per mole) and the keto-enol form (1075 Cal. per mole). The calculated value for the

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[126] A bimolecular reaction is one in which two molecules react.

[127] P. J. Wiezevich and A. H. Gleason, U. S. P. 1,998,404, April 16, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 3689; *Brit. Chem. Abs.* **B**, 1936, 442.

[128] G. H. Law, U. S. P. 2,019,983, Nov. 5, 1935, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1936, **30**, 487; *Brit. Chem. Abs.* **B**, 1936, 1195. Canadian P. 352,920, 1935; *Chem. Abs.*, 1935, **29**, 8008. British P. 410,394, 1934; *Brit. Chem. Abs.* **B**, 1934, 665; *Chem. Abs.*, 1934, **28**, 6160. French P. 761,731, 1934; *Chem. Abs.*, 1934, **28**, 4072.

[129] W. R. Aneus, A. H. Leckie, C. G. LeFevre, R. J. W. LeFevre and A. Wasserman, *J.C.S.*, 1935, 1751; *Chem. Abs.*, 1936, **30**, 1740; *Brit. Chem. Abs.* **A**, 1936, 191.

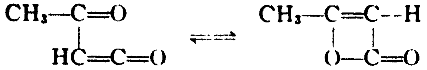
[130] Dipole moment is the product of the magnitude of the equal and opposite ionic charges and of the distance by which they are separated.

[131] Molecular refractivity may be expressed as

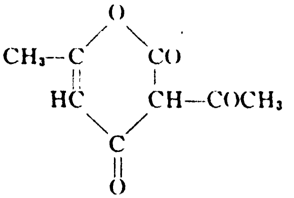
$$[R] = \frac{(n-1)}{d} M$$

where n is the index of refraction, d the density, and M is the molecular weight.

dienol form is somewhat lower (1049 Cal. per mole). On the other hand, Hurd and Williams[132] maintain that the structure of the dimer[133] of ketene may be represented as acetylketene or a resonance isomer[134] of this substance:



The calculated heat of formation of acetylketene was found to be 1086 Cal. per mole, which is in fairly close agreement with the value listed above. Furthermore, according to Hurd and Williams, the structure proposed by them would account for the further polymerization to the tetramer, which is dehydroacetic acid.



One suggested use for diketene is in the preparation of acetoacetanilide.[135] As an illustration, diketene is slowly added to a solution of aniline in toluene, maintained at 50 to 70°C. On cooling the reaction mixture to 20°C. a yield of the crystals separates, and on further cooling to 5°C. another crop of acetoacetanilide is secured. Subsequent evaporation of the mother liquor yields additional crystals of both acetanilide and acetoacetanilide from which the latter may be extracted with caustic soda solution.

Preparation of Higher Ketones

The acetone homologues are good solvents for many purposes. In the cellulose lacquer industry especially their higher boiling points make these ketones in some respects superior to acetone.[136] They have been prepared by the distillation of wood, the dry distillation of the calcium salts of the aliphatic acids, the oxidation of alcohols, the condensation of organic acid chlorides with hydrocarbons and the reaction of lower aliphatic ketones with aliphatic primary alcohols.

Preparation from Secondary Alcohols. *Methyl ethyl ketone*, $CH_3COCH_2CH_3$, is a colorless liquid of pleasant odor, boiling at 78.6°C. One method of preparation is by the oxidation of secondary butyl alcohol. Batalin and Sekretareva[137] reported an 88 per cent yield of the ketone by oxidizing *sec*-butanol at about 500°C. with the aid of a zinc oxide catalyst. The main fraction of the condensate, boiling from 78 to 81°C., had d_4^{20} 0.8057, $n_D^{15.9}$ 1.382. For producing a higher aliphatic ketone from a lower one a mixture of the latter with a lower aliphatic primary alcohol together with hydrogen or nitrogen may be led over a catalyst at 150 to 400°C. The contact agent suggested is alumina containing small proportions of copper, silver, cupric or cuprous oxide, silver oxide or molybdenum trioxide. In this manner acetone and methanol give methyl ethyl ketone, and methyl propyl ketone is prepared from ethanol and acetone.[138] Likewise, methyl amyl ketone results from butyl alcohol and acetone and higher ketones from ethanol and methyl ethyl ketone.

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[132] C. D. Hurd and J. W. Williams, *J.A.C.S.*, 1936, 58, 962; *Chem. Abs.*, 1936, 30, 5182.

[133] Note also Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935, 553.

[134] When a molecule has two alternative structures which have nearly the same energy content and a similar spatial arrangement, then a state of continuous and very rapid oscillation may occur between the two forms. Any such molecule is said to be in a state of resonance.

[135] G. H. Law, U. S. P. 1,982,675, Dec. 4, 1934, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, 29, 482. British P. 429,982, 1935; *Brit. Chem. Abs.* B, 1935, 761; *Chem. Abs.*, 1935, 29, 6907. French P. 781,167, 1935; *Chem. Abs.*, 1935, 29, 6252.

[136] Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, 1934.

[137] V. S. Batalin and E. V. Sekretareva, *Sintet. Kauchuk*, 1936, No. 1, 14; *Chem. Abs.*, 1936, 30, 4148. A commercial plant for the separation of methyl ethyl ketone from methyl propyl ketone has been described by I. F. Chistov and A. M. Terekhov, *Lesokhimicheskaya Prom.*, 1934, 3, No. 11, 15; *Brit. Chem. Abs.* B, 1935, 1036; *Chem. Abs.*, 1935, 29, 2911. The density, vapor pressure and index of refraction of methyl ethyl ketone as functions of temperature are discussed by W. A. Felsing, L. Shofner and N. B. Garlock, *J.A.C.S.*, 1934, 56, 2252; *Chem. Abs.*, 1935, 29, 670; *Brit. Chem. Abs.* A, 1935, 22.

Methyl propyl ketone, $CH_3COC_3H_7$, may also be secured by the catalytic dehydrogenation of *sec.*-pentanol.[139] The alcohol is heated to 400°C. in contact with an alloy of 60 per cent copper, 38.5 per cent zinc and 1.5 per cent tin.[140] Other ketones result on similar treatment of different secondary alcohols. Methyl propyl ketone is said to result from the treatment of a mixture of acetone and ethanol at 150-400°C. with a mixed catalyst, e.g., magnesium, 89; aluminum, 8; copper, 2; and silver, 1 per cent.[140a] Higher ketones may also be prepared by condensing ketones with aldehydes and subjecting the product to further treatment.[141] With an alkaline catalyst, ethylhexaldehyde and acetone yield undecyl ketol, which, on losing water, forms an unsaturated undecylene ketone, $C_4H_9CH(C_2H_5)CH=CHCOCH$, boiling at 229°C. Hydrogenation gives a saturated ketone boiling at 93°C.

Di-*n*-propyl ketone, $C_4H_9COC_4H_9$, which boils at 143.5°C., is a solvent for both cellulose nitrate and acetate and also for rubber, natural and synthetic resins, and for linseed and castor oils. In addition, it is free from toxicity and has a pleasant sweetish odor.[142] To convert *n*-butanol to dipropyl ketone, the alcohol may be subjected at 400 to 500°C. to the action ot oxygen compounds of such metals as iron, copper and manganese mixed with oxides of zinc, magnesium or calcium. Subatmospheric pressures are recommended.[143] Dipropyl ketone may be produced indirectly from the fermentation of carbohydrates.[144] The latter, when inoculated with a lactic ferment, will produce lactic acid, (α-hydroxypropionic acid). The fermentation is effected in the presence of calcium carbonate to form calcium lactate. The liquid is then inoculated with a butyric ferment to convert the lactate to calcium butyrate. The latter, after recovery in a concentrated form, is treated with sulphuric acid to liberate butyric acid, which may be collected by distillation. Passage of the fatty acid at 350°C. over thorium oxide deposited on pumice causes conversion to dipropyl ketone.

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[138] British P. 400,384, 1933, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1934, **28**, 2013; *Brit. Chem. Abs.* **B**, 1934, 10. German P. 616,016, 1935; *Chem. Abs.*, 1935, **29**, 8002. For methods of drying ketones, see W. H. Shiffler and R. C. Mithoff, U. S. P. 2,000,043, May 7, 1935, to Standard Oil Co. of Calif.; *Brit. Chem. Abs.* **B**, 1936, 537; *Chem. Abs.*, 1935, **29**, 4021. *Cf.* A. A. Pryanishnikov, Russian P. 31,939, 1933; *Chem. Abs.*, 1934, **28**, 3425.

[139] F. M. Archibald and C. M. Beamer, U. S. P. 2,028,267, Jan. 21, 1936, to Standard Alcohol Co.; *Chem. Abs.*, 1936, **30**, 1805; *Brit. Chem. Abs.* **B**, 1937, 118. For a discussion of the methods of determining methyl propyl ketone, see A. A. Pryanishnikov, *Lesokhimicheskaya Prom.*, 1933, **2**, No. 3, 27; *Brit. Chem. Abs.* **B**, 1935, 663; *Chem. Abs.*, 1935, **29**, 1749.

[140] For the separation of methyl propyl ketone, see J. A. van Melsen and S. L. Langedijk, U. S. P. 2,010,384, Aug. 6, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 6252. British P. 417,101, 1934, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1934, 1050; *Chem. Abs.*, 1935, **29**, 1100. French P. 770,622, 1934; *Chem. Abs.*, 1935, **29**, 476. A. A. Pryanishnikov, Russian P. 31,010, 1933; *Chem. Abs.*, 1934, **28**, 3425.

[140a] O. Fuchs, E. Naujoks and W. Querfurth, U. S. P. 2,064,254, Dec. 15, 1936; *Chem. Abs.*, 1937, **31**, 703.

[141] French P. 786,734, 1935, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1936, **30**, 734.

[142] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

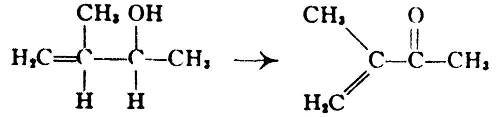
[143] G. Bloomfield, L. C. Swallen and F. M. Crawford, U. S. P. 1,978,404, Oct. 30, 1934, to Commercial Solvents Corp.; *Chem. Abs.*, 1935, **29**, 177.

[144] H. Hibbert, U. S. P. 1,283,183, Oct. 29, 1918; *Chem. Abs.*, 1919, **13**, 187; *J.S.C.I.*, 1919, **38**, 91A.

OTHER KETONES FROM ALCOHOLS

Dehydrogenation of menthol by conducting a mixture of its vapor with steam over catalysts at 185°C. is said to give a 96 per cent yield of methone.[145] Also, borneol may be converted into camphor by dehydrogenation in the liquid phase.[146] For example, the alcohol is mixed with benzene in the ratio 3:1 by weight and the two placed in a closed vessel with a small proportion of nickel. The reaction chamber is then heated to 200°C. under a pressure of 100 lbs. per sq. in. Oxidation of a secondary alicyclic alcohol, such as cyclohexanol, to the corresponding ketone is said to be possible by passage of the former in vapor phase, with oxygen, over a catalyst of metallic silver at temperatures between 500 and 600°C.[147]

Unsaturated Ketones from Alcohols. Dehydrogenation or oxidation of unsaturated alcohols with the aid of catalysts leads to the production of unsaturated ketones. Groll[148] converted 2-methyl-1-butene-3-ol into methyl isopropenyl ketone by passing the alcohol over brass spelter in a copper tube heated above 250°C.



Similar treatment of 2-methyl-2-butene-4-ol gave β,β-dimethylacrolein. Silica gel and active alumina when used as catalysts in this treatment are reported to give saturated ketones in place of the unsaturated.[149] Thus, phenylisopropenylcarbinol, $C_6H_5CH(OH)C(CH_3)=CH_2$, passed over active alumina, would give phenyl isopropyl ketone. On the other hand, the same unsaturated alcohol is said to give the corresponding unsaturated ketone by oxidation at about 410°C. in the presence of vanadyl sulphate supported on silica gel.[150]

KETONES FROM PARAFFINS AND CYCLOPARAFFINS

An interesting observation in the field of organic synthesis is that the Friedel-Crafts reaction is in many cases applicable to olefins, paraffins and cycloparaffins. Thus, with the aid of condensing agents, organic acid chlorides will react with these types of hydrocarbons to yield ketones.

By the condensation of *n*-pentane with acetyl chloride in the presence of aluminum chloride, Hopff[151] obtained a ketone which he considered to be 2-acetylpentane (methyl *n*-propyl acetone), $CH_3COCH(CH_3)CH_2CH_2CH_3$. However, Nenitzescu and Chicos[152] report that the main product is methylisopropylacetone (3,4-dimethylpentan-2-one) accompanied by some methylisopropenylacetone (3,4-

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[145] H. Sandkuhl, German P. 608,622, 1935, to Rheinische Kampfer-Fabrik G.m.b.H.; *Chem. Abs.*, 1935, **29**, 5125.

[146] C. O. Henke, U. S. P. 1,933,215, Oct. 31, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1934, 873; *Chem. Abs.*, 1934, **28**, 483. French P. 736,087, 1932; *Chem. Abs.*, 1933, **27**, 1361.

[147] G. D. Graves, U. S. P. 2,015,751, Oct. 1, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 8002; *Brit. Chem. Abs.* B, 1936, 1143.

[148] H. P. A. Groll, British P. 435,494, 1935, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* B, 1935, 1130; *Chem. Abs.*, 1936, **30**, 1385. French P. 772,908, 1934; *Chem. Abs.*, 1935, **29**, 1434.

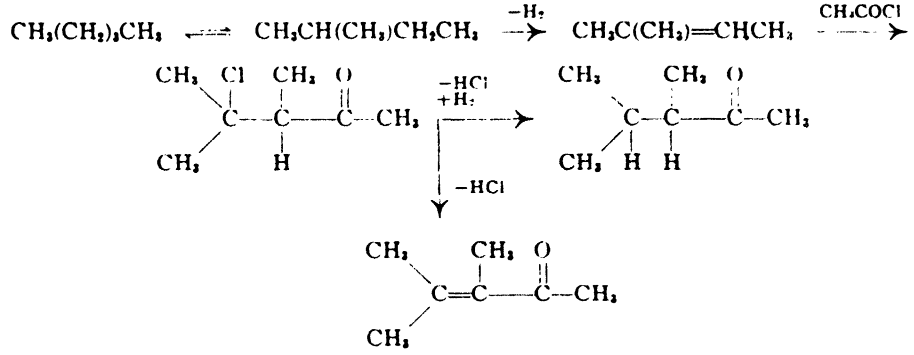
[149] H. P. A. Groll and C. J. Ott, British P. 441,334, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 4511.

[150] H. P. A. Groll and H. W. de Jong, British P. 436,840, 1935; *Chem. Abs.*, 1936, **30**, 2200.

[151] H. Hopff, *Ber.*, 1931, **64**, 2739; *Chem. Abs.*, 1932, **26**, 1236; *Brit. Chem. Abs.* A, 1932, 44. See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934, 417.

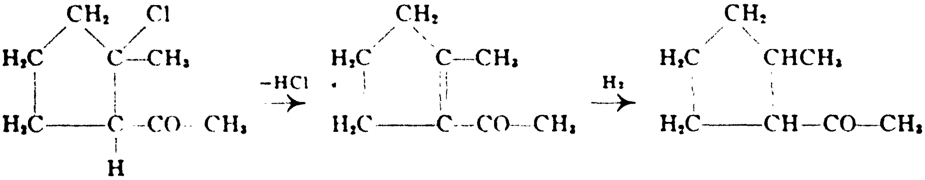
[152] C. D. Nenitzescu and I. Chicos, *Ber.*, 1935, **68**, 1584; *Brit. Chem. Abs.* A, 1935, 1221; *Chem. Abs.*, 1935, **29**, 7279.

dimethyl-3-penten-2-one). To explain this reaction, initial isomerization of *n*-pentane to 3-methylbutane was postulated. The following scheme was proposed:



In a similar manner *n*-hexane and acetyl chloride gave 4-methyl-3-ethyl pentan-2-one and 4-methyl-3-ethyl-3-penten-2-one.

A somewhat analogous behavior has been found in the action of aluminum chloride and acetyl chloride on cyclohexane.[153] The reported mechanism is that methylcyclopentane is first formed, which loses hydrogen to yield a methylcyclopentene. The latter adds acetyl chloride to give a chloroketone, which in the presence of inactive aluminum chloride splits out hydrogen chloride, forming 1-methyl-2-acetylcyclopentene. With active aluminum chloride, however, hydrogenation also takes place to 1-methyl-2-acetylcyclopentane.



In an investigation of the constituents of commercial petroleum benzine, treatment with aluminum chloride and acetyl chloride gave large yields of cyclic ketones, indicating the presence of considerable amounts of alkylcyclopentanes in the fractions.[154] Cyclohexane hydrocarbons were converted to benzenoid hydrocarbons by dehydrogenation, and aromatic hydrocarbons were removed by oleum treatment before the fractions were subjected to the aluminum chloride-acetyl chloride reaction. In each case unsaturated ketones were first obtained (20 to 60 per cent yields) which could be reduced to saturated ketones. Further hydrogenation gave cycloparaffins.

According to Schaarschmidt[155] saturated paraffin and cycloparaffin hydrocarbons may be converted to corresponding ketones by treatment with phosgene and aluminum halides at temperatures of +5 to —15°C. Thus, isopentane will yield diisoamyl ketone in the presence of aluminum chloride. If *n*-pentane is also present in the original reaction mixture, it may be separated and treated with phosgene and either the bromide or iodide of aluminum. It has also been proposed to employ carbon monoxide in place of phosgene.[156] Thus, isopentane or methylcyclohexane may be treated with carbon monoxide and aluminum bromide at 0 to 20°C. under pressure. The resulting intermediate complex is decomposed with cold water or ice to yield ketones.

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[153] C. D. Nenitzescu and G. G. Vantu, *Bull. soc. chim.*, 1935, (5) **2**, 2209; *Chem. Abs.*, 1936, **30**, 1749; *Brit. Chem. Abs.* **A**, 1936, 205. See also H. Hopff, *Ber.*, 1932, **65**, 482; *Brit. Chem. Abs.* **A**, 1932, 514.

[154] N. D. Zelinskii and L. Leder-Packendorff, *Ann.*, 1935, **518**, 260; *Brit. Chem. Abs.* **B**, 1935, 836; *Chem. Abs.*, 1935, **29**, 6401. N. D. Zelinskii and E. M. Tarassova, *Ann.*, 1934, **508**, 115; *Chem. Abs.*, 1934, **28**, 3384; *Brit. Chem. Abs.* **A**, 1934, 295.

[155] A. Schaarschmidt, U. S. P. 1,995,752 and 1,995,753, Mar. 26, 1935, to Antares Trust Registered; *Chem. Abs.*, 1935, **29**, 3349; *Brit. Chem. Abs.* **B**, 1936, 442. Swiss P. 165,822, 1934; *Chem. Abs.*, 1934, **28**, 2724.

The reaction of selenious acid or anhydride with cyclic compounds containing the group $CH=CHCH_2$ is said to give unsaturated ketones.[157] A solvent, e.g., benzene, may be employed for the selenium compound and the reaction carried out under pressure. Methylcyclohexene, 1-menthene, 3-menthene, α-pinene, β-pinene, dipentene and eugenol may be treated in this manner.

Higher Ketones from Carboxylic Acids

It is reported that simple olefin hydrocarbons may be converted into aliphatic carboxylic acids by direct combination with carbon monoxide and steam under high pressure according to the reaction,

$$RR'C{=}CR''R''' + H_2O + CO \longrightarrow CHRR'\cdot CR''R'''COOH$$

where R, R', R'' and R''' represent hydrogen atoms or alkyl radicals.[158] The reaction is said to be catalyzed by volatile halides, such as hydrogen chloride,[159] by active carbon and ammonium chloride,[160] and by boron phosphate.[161] Thus, propionic acid may be obtained from ethylene by the above reaction at 350°C. and 700 atmospheres. Carboxylic acids of this type may be treated catalytically to give ketones, so that the two types of reaction in conjunction form an indirect method of making ketones from olefins. Practically theoretical yields of diethyl ketone have been reported[162] from treatment of propionic acid vapor at 300-370°C. in the presence of a thoria aerogel catalyst.[163] In the procedure, the acid was distilled into a catalyst chamber consisting of two concentric glass tubes sealed at the ends so that a 4 mm. space was formed between them (see Fig. 117). The lower 5 cm. of the annular space was filled with broken pumice, and above that was placed 18 g. of the catalyst. The balance of the space was filled with pumice to aid in bringing the entering gases to the required temperature before reaching the aerogel. Heaters were placed inside as well as outside of the catalyst chamber to obtain a maximum heating surface. The yields of diethyl ketone varied from 94.5 to 100 per cent, depending on the temperature (300 to 374°C.) and rate of flow of vapor (3.0 to 12.3 g. per minute). In a similar manner, 94.4 to 100 per cent yields of di-*n*-butyl ketone and 92.8 to 100 per cent yields of di-*n*-heptyl ketone were obtained from *n*-valeric acid and from caprylic acid, respectively. Other catalysts for the decomposition of acids to ketones include oxides of thorium and cerium.[164]

Also, oleic acid is said to be converted into oleone, a waxy ketone, in 83 per cent yield by contact with reduced iron or ferric oxide at 200-320°C. in the presence of a non-oxidizing gas such as carbon dioxide.[165] A proposed method for the preparation of aldehydes and ketones from petroleum acids consists in converting the latter into α-bromo acids and thence into α-hydroxy acids which are subjected to dry distillation.[166]

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[156] A. Schaarschmidt, U. S. P. 2,037,050, April 14, 1936, to Antares Trust Registered; *Chem. Abs.*, 1936, 30, 3440.

[157] E. Schwenk and E. Borgwardt, German P. 582,545, 1933, to Schering-Kahlbaum A.-G.; *Chem. Abs.*, 1934, 28, 779. French P. 751,807, 1933; *Chem. Abs.*, 1934, 28, 779.

[158] G. B. Carpenter, U. S. P. 1,924,766, Aug. 29, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 5340; *Brit. Chem. Abs.* B, 1934, 534.

[159] G. B. Carpenter, U. S. P. 1,924,763, Aug. 29, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 5340; *Brit. Chem. Abs.* B, 1934, 534.

[160] A. T. Larson and W. E. Vail, U. S. P. 1,924,765, Aug. 29, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 5340; *Brit. Chem. Abs.* B, 1934, 534.

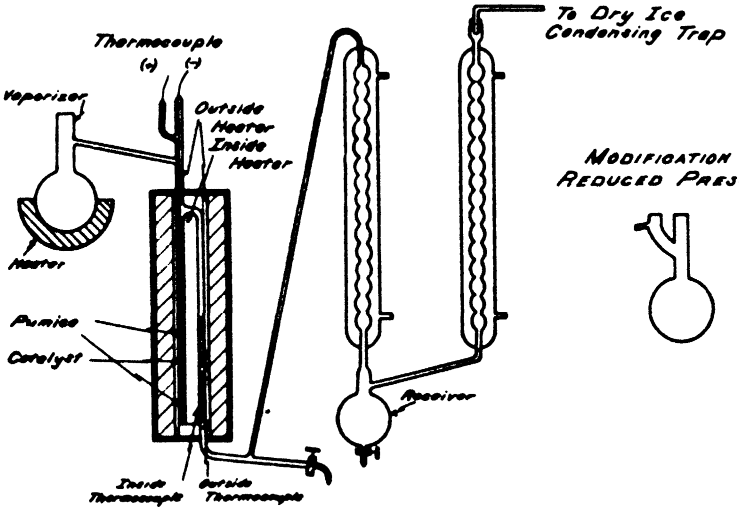
[161] W. E. Vail, U. S. P. 1,924,764, Aug. 29, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 5340; *Brit. Chem. Abs.* B, 1934, 534.

[162] S. S. Kistler, S. Swann, Jr., and E. G. Appel, *Ind. Eng. Chem.*, 1934, 26, 388; *Chem. Abs.*, 1934, 28, 3845; *Brit. Chem. Abs.* A, 1934, 609.

[163] An aerogel is a colloid in which the phases are solid and vapor.

[164] German P. 630,909, 1936, to Maison Camus Duchemin (Soc. anon.); *Chem. Abs.*, 1937, 31, 110.

Condensation of aromatic hydrocarbons with acyl chlorides by action of Friedel-Craft's condensing agents furnishes aralkyl ketones. In the case of monoalkyl benzenes the acyl group is said to be substituted in the para position.[167] The following example illustrates the preparation of *p*-*n*-propylpropiophenone. A mixture of 204 g. of *n*-propylbenzene and 150 g. of propionyl chloride was slowly added to a stirred suspension of 150 g. of aluminum chloride incorporated in 200 cc. of carbon disulphide. After the evolution of hydrogen chloride ceased, 30 g. of aluminum chloride were added and stirring continued. In the synthesis of methyl naphthyl ketones from naphthalene and acetyl chloride, Rivkin[168] found that less resinous by-products were formed if the aluminum chloride was added slowly to the mixture of reactants in a solvent. The condensations were effected in a closed copper container provided with a mechanical stirrer. Optimum yields were obtained when concentrated solutions were employed and the temperature maintained around 10°C. In one case, 130 g. of naphthalene and 80 g. of acetyl chloride were dissolved in 1000 g. of benzene. To 300 g. of this solution were added 150 g. of aluminum chloride, and after a few minutes of stirring, the remaining portions of the reactants were introduced dropwise, the temperature being kept between 10 and 13°C. At the end of 6 hours a complex compound separated from the solu-



Courtesy Industrial and Engineering Chemistry

FIG. 117.—Apparatus for Production of Ketones from Organic Acids, Employing Aerogel Catalysts. (S. S. Kistler, S. Swann, Jr., and E. G. Appel)

tion. This complex was decomposed by immersing in ice water and on fractionation yielded 69.5 g. of methyl naphthyl ketone, b.p. 156-160°C. under 9 mm. pressure. With the same amounts of naphthalene and acetyl chloride dissolved in 500 g. of nitrobenzene and the temperature between 8 and 10°C., 154 g. of methyl naphthyl ketone were secured in 9 hours. Instead of acyl chlorides, the corresponding carboxylic acid or acid anhydride may be employed in this type of reaction, provided that sufficient condensing agent is present. Thus, treatment of a mixture of 1 mole of acetic acid and 2 moles of toluene with 2.5 moles of aluminum chloride in an air stream at 105°C. was said to give an 80 per cent yield of *p*-methylacetophenone.[169] Condensation of 1 mole of acetic anhydride with 3 moles of toluene aided by 3 moles of aluminum chloride at 100°C. afforded a 75-85 per cent yield of 4-methylacetophenone.[170] Employment of an aluminum hydrosilicate catalyst at temperatures of 100-350°C. has been proposed for an analogous condensation of aromatic hydrocarbons with aromatic carboxylic acids.[171] Thus, *β*-naphthyl phenyl ketone may be produced from naphthalene and benzoic acid. The reaction is stated to be applicable to the production of ketones from heterocyclic compounds (except compounds of the pyridine series), including indole, thiophene and thionaphthene. Bruson and Stein[172] describe a method of producing alkylated aromatic ketones by reaction of an acylating agent with a mixture of a non-alkylated hydrocarbon, such as benzene, and an aliphatic halide in the presence of a condensing agent. In this manner the aliphatic chloride is said to interact with the cyclic compound to form a homologue of benzene. The latter then combines with the acetylating agent to produce the ketone. For example, benzene, amyl chloride and acetyl chloride may be treated with aluminum chloride at 100°C. to furnish amylphenyl methyl ketone, which boils at 121-123°C. at 3 mm. pressure. The latter compound has been suggested as a solvent in paint removers and as a lacquer ingredient.

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[165] D. K. Tressler, U. S. P. 1,941,640, Jan. 2, 1934, to Mathieson Alkali Works; *Chem. Abs.*, 1934, **28**, 1715.

[166] A. E. Chichibabin, M. M. Katznelson and G. V. Chelintzev, Russian P. 31,440, 1933; *Chem. Abs.*, 1934, **28**, 3227.

[167] G. Baddeley and J. Kenner, *J.C.S.*, 1935, 303; *Brit. Chem. Abs.* A, 1935, 612; *Chem. Abs.*, 1935, **29**, 3323.

[168] S. M. Rivkin, *J. Gen. Chem. (U.S.S.R.)*, 1935, **5**, 277; *Chem. Abs.*, 1935, **29**, 5102.

PROPERTIES AND USES OF HIGHER KETONES

The homologues of acetone, in general, undergo the same reactions as the simplest ketone. They form addition products with hydrogen cyanide and sodium hydrogen sulphite, condensation products with hydroxylamine, hydrazine and phenylhydrazine, and may be oxidized to acids or reduced to alcohols.

Decomposition by Ultraviolet Radiation. The photochemical decompositions of methyl ethyl and methyl butyl ketone have been studied to determine the mechanism of each of these reactions.[173] The apparatus consisted of a quartz flask attached to a water-cooled condenser and spherical bulb (see Fig. 118). By completely evacuating the system and cooling the quartz flask in liquid air a sample of the ketone could be distilled into the flask from a side reservoir. The liquid air was then removed and the ketone allowed to reflux by slight heating. The vapor in the neck of the flask was illuminated by a vertical mercury lamp, furnishing lines of 3000-2200Å. The products of the photodecomposition were collected in the spherical bulb, from which samples were easily drawn off for analysis. In the case of methyl ethyl ketone it was concluded the reaction proceeds through two courses, one leading to ethane, propane, butane and carbon monoxide, the other to ethylene and acetaldehyde.

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[169] P. H. Groggins and R. H. Nagel, U. S. P. 1,966,797, July 17, 1934, to the Secretary of Agriculture, U.S.A.; *Brit. Chem. Abs.* B, 1935 443; *Chem. Abs.*, 1934, **28**, 5469.

[170] P. H. Groggins, U. S. P. 1,991,743, Feb 19, 1935, to the Secretary of Agriculture, U.S.A.; *Chem. Abs.*, 1935, **29**, 2175; *Brit. Chem. Abs.* B, 1936, 91. *Cf.* P. H. Groggins and R. H. Nagel, U. S. P. 1,997,213, April 9, 1935, to the Secretary of Agriculture, U.S.A.; *Chem. Abs.*, 1935, **29**, 3688; *Brit. Chem. Abs.* B, 1936, 442.

[171] S. Skraup, U. S. P. 1,995,402, Mar. 26, 1935, to Rheinische Kampfer-Fabrik G.m.b.H.; *Chem. Abs.*, 1935, **29**, 2974. German P. 621,454, 1935; *Chem. Abs.*, 1936, **30**, 1066.

[172] H. A. Bruson and O. Stein, U. S. P. 2,004,069, June 4, 1935, to Röhm & Haas Co.; *Chem. Abs.*, 1935, **29**, 4773.

[173] R. G. W. Norrish and M. E. S. Appleyard, *J.C.S.*, 1934, 874; *Chem. Abs.*, 1934, **28**, 5758; *Brit. Chem. Abs.* A, 1934, 852.

$$3CH_3COC_2H_5 \longrightarrow C_2H_6 + C_3H_8 + C_4H_{10} + 3CO$$
$$CH_3COC_2H_5 \longrightarrow C_2H_4 + CH_3CHO$$

With methyl butyl ketone the decomposition may be represented as:

$$CH_3CH_2CH_2CH_2COCH_3 \longrightarrow CH_3CH{=}CH_2 + CH_3COCH_3$$

These results were somewhat unexpected, in view of the fact that the carbonyl group is the one which absorbs the lines between 3500Å. and 2000Å. However, the carbonyl group apparently was not disrupted in the photochemical change since no oxygen was found in the decomposition products. It was assumed that the energy passes in whole or in part from the carbonyl link to some point in the hydrocarbon chain, with the result that carbon monoxide and a mixture of paraffins are produced in nearly equivalent proportion.

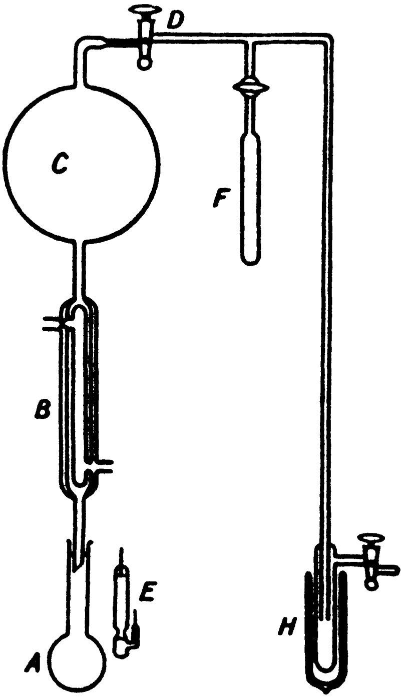

FIG. 118.
Apparatus for Photochemical Decomposition of Ketones. (R. G. W. Norrish and M. E. S. Appleyard)

A. Quartz flask
B. Water condenser
C. Liter globe
D. Stopcock
E. Mercury lamp
F. Trap
H. Trap for collecting fractions

Courtesy Journal of the Chemical Society

$$3CH_3COC_2H_5 \longrightarrow 3CH_3 + 3C_2H_5 + 3CO$$
$$3CH_3 + 3C_2H_5 \longrightarrow C_2H_6 + C_3H_8 + C_4H_{10}$$

Also, the photochemical decomposition of di-*n*-propyl ketone follows a mechanism similar to that proposed for methyl butyl ketone.[174]

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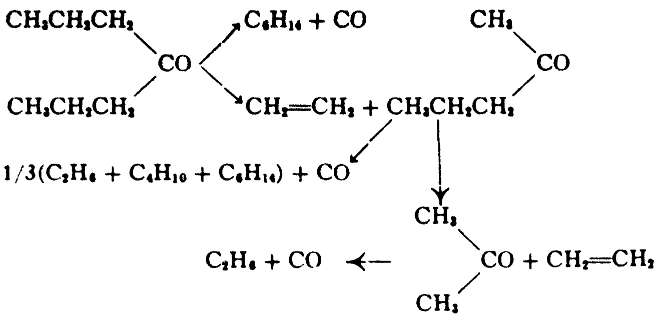
[174] C. H. Bamford and R. G. W. Norrish, *J.C.S.*, 1935, 1504; *Chem. Abs.*, 1936, 30, 1304; *Brit. Chem. Abs.* A, 1935, 1468. R. G. W. Norrish, *Acta Physicochim. U.R.S.S.*, 1935, 3, 171; *J. Phys. Chem.* (*U.S.S.R.*), 1936, 7, No. 2; *Chem. Abs.*, 1936, 30, 2493. See also T. G. Pearson and R. H. Purcell, *Nature*, 1935, 136, 221; *Brit. Chem. Abs.* A, 1935, 1221; *Chem. Abs.*, 1935, 29, 7277.



In all cases the break in the hydrocarbon chain was found to occur between the carbon atoms lying in positions a and β to the carbonyl group. It was therefore concluded that there is some sort of resonance between the carbonyl group and the carbon to carbon link in the a or β position, as a result of which the electronic energy of excitation of the former can be readily transferred to the latter. That free radicals play a part in the photochemical decomposition of ketones is indicated by the apparent formation of the propyl radical from diisopropyl ketone.[174a]

In cyclohexanone, 10 per cent solutions of methyl butyl ketone and of di-*n*-propyl ketone irradiated at 20°C. gave 98 per cent yields of propene and ethylene, respectively. However, at 100°C. the propyl ketone also formed ethane and carbon monoxide.[174b] From the behavior in gaseous phase and in solution, two types of reaction mechanism were postulated; one having activated molecules with relatively long lives which can be readily extinguished by solvent molecules; the other having molecules with such short lives that there is no time for intervention of solvent molecules between activation and reaction.

Other studies of photoreactions in solution show that the nature of the solvent influences the type of products formed.[174c] Mercury arc irradiation of liquid acetone or of its solution in carbon tetrachloride showed evidence of a reaction in which no gas was evolved. Products of treatment in hexane solution were more unsaturated (to bromine) than those obtained from acetone alone. On the other hand, a solution of the ketone in benzene did not show a photoreaction. Alcohol formation in hexane solution and in cyclohexane was noted; the product in the former case was supposedly dimethyl-*n*-hexylcarbinol and, in the latter, cyclohexyldimethylcarbinol.

Oxidation. The action of oxidizing agents on ketones leads to carboxylic acids or keto-aldehydes. Both saturated and halogen-substituted ketones may be converted in this manner. For example, methyl ethyl ketone subjected, in the liquid phase, to the action of gaseous oxygen at 75 to 105°C. under 4 atmospheres pressure is said to give acetic acid.[175] A catalyst consisting of a mixture of ferrous acetate and acetic acid is suggested. In the same manner, methyl isopropyl ketone is converted to a mixture of acetic and formic acids, cyclohexanone to adipic acid, and acetophenone to benzoic and formic acids. Oxidation of ketones in the presence of copper at a temperature of 350°C. is reported to give polyketones and keto-aldehydes rather than acids.[176]

[174a] H. H. Glazebrook and T. G. Pearson, *J.C.S.*, 1936, 1777; *Chem. Abs.*, 1937, 31, 1356.

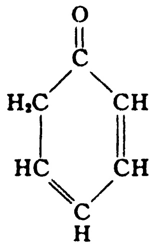
[174b] R. G. W. Norrish and C. H. Bamford, *Nature*, 1936, 138, 1016; *Chem. Abs.*, 1937, 31, 1703; *Brit. Chem. Abs.* A, 1937, 1, 91.

[174c] E. J. Bowen and E. L. A. E. de la Praudiere, *J.C.S.*, 1934, 1503; E. J. Bowen and A. T. Horton, *ibid.*, 1936, 1685; *Chem. Abs.*, 1935, 29, 1012; 1937, 31, 1298; *Brit. Chem. Abs.* A, 1934, 1316; A, 1937, 1, 39.

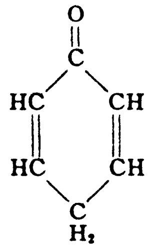
[175] W. Flemming and W. Speer, German P. 583,704, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1055. French P. 751,160, 1933; *Chem. Abs.*, 1934, 28, 1055. French P. 44,372, 1934; *Chem. Abs.*, 1935, 29, 2975. British P. 415,172, 1934; *Brit. Chem. Abs.* B, 1934, 953; *Chem. Abs.*, 1935, 29, 818.

[176] M. De Simo and S. H. McAllister, British P. 448,313, 1936, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* B, 1936, 780.

Electrolytic oxidation of cyclohexanone in dilute sulphuric acid, employing lead oxide and platinum electrodes, has produced maleic acid, a mixture of cyclic unsaturated ketones and a hydrocarbon, $C_{18}H_{12}$, presumed to be triphenylene.[177] It was thought that cyclohexanone first dehydrogenated to a mixture of two isomeric cyclohexadienones,



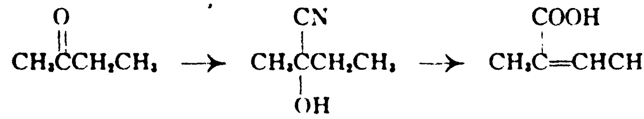
1,3-cyclohexadiene-6-one



1,4-cyclohexadiene-6-one

the latter being oxidized to maleic acid. Condensation of two molecules of 1,3-cyclohexadiene-6-one with elimination of water, and the corresponding condensation of three molecules of the ketone, gave respectively dicyclohexenedienehexenedienone and tricyclodihexenedienehexenedienone. Subsequent elimination of a molecule of water from the latter would explain the formation of triphenylene.

Addition of hydrogen cyanide to a ketone, and subsequent oxidation, yields an unsaturated acid. In one process, hydrogen cyanide is added to methyl ethyl ketone to form a ketone cyanohydrin which is then treated with sulphuric acid at 80-100°C. in the presence of hydroquinone. The latter is said to inhibit the formation of polymers of the cyanohydrin. The product is heated under reflux with water and ethanol to produce the ethyl ester of α-methyl crotonic acid together with the free acid.[178] In like manner acetophene may be converted into atropic



$$CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3 \longrightarrow CH_3\underset{\underset{OH}{|}}{\overset{\overset{CN}{|}}{C}}CH_2CH_3 \longrightarrow CH_3\overset{\overset{COOH}{|}}{C}{=}CHCH_3$$

acid (α-phenylacrylic acid) and ethyl atropate.

A halogen-substituted ketone may be treated with an oxidizing agent to produce halogen-substituted acids from which hydroxy acids may be obtained. Thus, lactic acid may be secured from α-chloroethyl methyl ketone by this means.[179] In the procedure, concentrated nitric acid is blown, together with air, through a capillary tube into a well-stirred mixture of α-chloroethyl methyl ketone, chloropropionic acid and water maintained at 80-100°C. The products of the oxidation are said to be α-chloropropionic acid and small proportions of acetic acid and 1,1,1-dinitrochloroethane. Fractional distillation is employed to separate the chloropropionic acid, which boils at 186°C. The latter may be treated with aqueous caustic soda and heated in an autoclave at 130°C. for a period of 2 hours to form lactic acid (α-hydroxy propionic acid). The oxidation and subsequent hydrolysis may be represented as

$$CH_3CHClCOCH_3 \longrightarrow CH_3CHClCOOH \longrightarrow CH_3CH(OH)COOH$$

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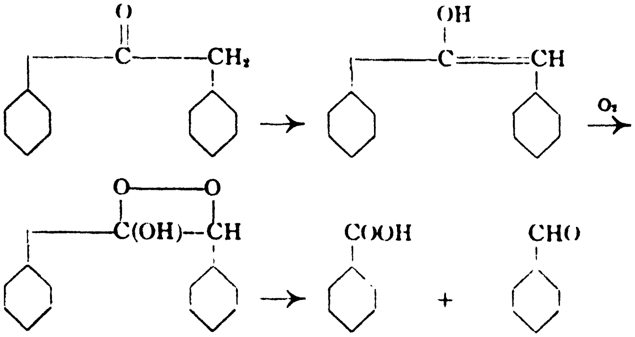
[177] F. Pirrone, *Gazz. chim. ital.*, 1936, 66, 244; *Chem. Abs.*, 1937, 31, 1371.

[178] J. W. C. Crawford, British P. 446,908, 1936, to Imperial Chemical Industries Ltd.; *Chem. Abs.*, 1936, 30, 6763; *J. Inst. Pet. Tech.*, 1936, 22, 368A.

[179] M. De Simo and C. C. Allen, U. S. P. 2,051,470, Aug. 18, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, 30, 6764. British P. 447,876, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, 30, 7124; *J. Inst. Pet. Tech.*, 1936, 22, 368A. French P. 797,943, 1936; *Chem. Abs.*, 1936, 30, 7124.

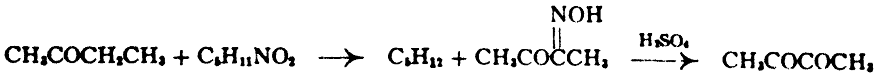
It is reported that halogen-substituted ketones containing two aromatic rings are autoxidized on exposure to air.[180] In one case benzyl-2-chlorophenyl ketone, which is a liquid, on standing slowly solidified and acquired a strong odor of benzaldehyde. The latter substance and, in addition, *o*-chlorobenzoic acid were isolated from the solid product. The suggested mechanism for the autoxidation was given as



Electrolytic Reduction. The electrolytic reduction of ketones has been reported to lead to the formation of straight-chain saturated hydrocarbons.[181] For example, a high yield of pentane is said to be obtained when 70 g. of methyl propyl ketone are dissolved in 70 cc. of 39 per cent sulphuric acid and reduced at 55-60°C., employing a cathode of cadmium and a current of 5 amperes.

Miscellaneous Reactions. Ketones containing only ethyl groups or higher react with zinc and organic halides to form metallic compounds which on hydrolysis yield tertiary alcohols.[182] Thus, dipropyl ketone, zinc and ethyl iodide give ethyl dipropyl carbinol. In like manner triethyl carbinol is made from diethyl ketone.

The action of aqueous solutions of nitrites upon methyl ethyl ketone has been utilized to prepare biacetyl.[182a] For example, the ketone mixed with amyl nitrite in the molecular ratio 1:2 and heated to 35-50°C. gives isonitrosoethyl methyl ketone. Subsequent treatment with dilute sulphuric acid and steam-distillation yields biacetyl.



$$CH_3COCH_2CH_3 + C_5H_{11}NO_2 \longrightarrow C_5H_{12} + CH_3CO\overset{\overset{NOH}{\|}}{C}CH_3 \xrightarrow{H_2SO_4} CH_3COCOCH_3$$

The effect of phosphorus pentachloride upon methyl ethyl ketone has been studied by Charpentier.[183] The reaction yielded 60 per cent of 2,2-dichlorobutane, b.p., 102°C., and 40 per cent of a liquid boiling between 60 and 65°C. The latter proved to be a mixture which could not be completely separated by repeated distillation. However, the two end fractions (b.p. 58.5-58.9°C. and b.p. 65-66°C.) were oxidized by potassium permanganate, the lower fraction furnishing propionic acid and the higher one acetic acid. It was therefore concluded that a portion of the 2,2-dichlorobutane lost a molecule of hydrogen chloride to form both 2-chloro-1-butene and 2-chloro-2-butene.

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[180] S. S. Jenkins, *J.A.C.S.*, 1935, 57, 2733; *Chem. Abs.*, 1936, 30, 1782; *Brit. Chem. Abs.* A, 1936, 333.

[181] S. Swann, Jr., and J. Feldman, *Trans. Electrochem. Soc.*, 1934, 67, 19; *Brit. Chem. Abs.* A, 1935, 310; *Chem. Abs.*, 1935, 29, 54. S. Swann, Jr., L. F. Deditius and W. A. Pyhrr, *Trans. Electrochem. Soc.*, 1935, 68, 89; *Chem. Abs.*, 1935, 29, 6150; *Brit. Chem. Abs.* A, 1935, 1224.

[182] A. Saytzeff, *J. pr. Chem.*, 1885, 31 (2), 319; *J.C.S.*, 1885, 48, 881.

[182a] J. Pien, J. Baisse and R. Martin, *Lait*, 1936, 16, 119; *Chem. Abs.*, 1936, 30, 3362. *Cf.* H. Puttfarcken, German P. 597,256, 1934, to Vanillin-Fabrik G.m.b.H.; *Chem. Abs.*, 1934, 28, 5083.

[183] P. Charpentier, *Bull. soc. chim.*, 1934, 1 (5), 1407; *Chem. Abs.*, 1935, 29, 1771; *Brit. Chem. Abs.* A, 1935, 62.

Treatment of diethyl ketone with a methanolic solution of calcium hypochlorite is reported to give a mixture of chloroform, acetic acid and propionic acid.[184] The reaction was explained on the basis of enolization of the ketone by alkali followed by reaction of the enolic hydroxyl group with calcium hypochlorite and isomerization to the α-chloroketone. The latter then follows the same procedure to form an α,α-dichloroketone.

$$\mathrm{CH_3CH_2COCH_2CH_3} \xrightarrow{\mathrm{Ca(OH)_2}} \mathrm{CH_3CH_2C(OH){=}CHCH_3} \xrightarrow{\mathrm{Ca(OCl)_2}}$$
$$\mathrm{CH_3CH_2COCl{=}CHCH_3} \longrightarrow \mathrm{CH_3CH_2COCHClCH_3} \longrightarrow \mathrm{CH_3CH_2COCCl_2CH_3}$$

USES OF HIGHER KETONES

Because of their selective solvent properties, some of the higher ketones have been recommended for dewaxing lubricating oil. The general procedure consists of mixing the ketone with the oil and cooling to between −10 and −23°C., in which range the ketone has excellent solvent action on the oil and substantially none on the wax. The latter is then removed by filtration or centrifuging. Among the ketones suggested for this purpose are included methyl ethyl,[185] a mixture of methyl ethyl and dipropyl,[186] methyl isobutyl,[187] acetophenone[188] and cyclohexanone.[189] Some ketones have been recommended as solvents for resins and cellulose acetate and nitrocellulose lacquers, among them being methyl ethyl ketone, methyl butyl ketone, methyl propyl ketone, methyl amyl ketone[190] and cyclohexanone.[191] Also, the higher ketones are employed in some cases in reactions with other substances, as, for example, phenols, to form synthetic resins.[192]

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[184] I. F. Suknevich and A. A. Chilingaryan, *Ber.*, 1936, **69**, 1537; *Brit. Chem. Abs.* **A**, 1936, 963; *Chem. Abs.*, 1936, **30**, 5936.

[185] B. Y. McCarty and W. E. Skelton, U. S. P. 1 969,670, Aug. 7, 1934, to Texas Co.; *Chem. Abs.*, 1934, **28**, 6297; *Brit. Chem. Abs.* **B**, 1935, 617; *J. Inst. Pet. Tech.*, 1934, **20**, 540A. G. Weber, *Oil and Gas J.*, 1936, **35** (9), 46; *J. Inst. Pet. Tech.*, 1936, **22**, 510A; *Chem. Abs.*, 1936, **30**, 7829.

[186] E. C. Knowles, U. S. P. 2,054,429, Sept. 15, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 7839; *J. Inst. Pet. Tech.*, 1936, **22**, 549A.

[187] H. H. Gross and W. E. Overbaugh, U. S. P. 2,047,412, July 14, 1936, to Texas Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 456A; *Chem. Abs.*, 1936, **30**, 6184. French P. 796,168, 1936, to Texaco Development Corp.; *Chem. Abs.*, 1936, **30**, 5779. Canadian P. 360,567, 1936; *Chem. Abs.*, 1936, **30**, 7839.

[188] E. R. Birkhimer, U. S. P. 2,026,812, Jan. 7, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 161A.

[189] E. F. Pevere, U. S. P. 2,003,667, June 4, 1935, to Texas Co.; *Brit. Chem. Abs.* **B**, 1936, 534; *Chem. Abs.*, 1935, **29**, 4931. French P. 780,468, 1935, to Texaco Development Corp.; *Chem. Abs.*, 1935, **29**, 6043.

[190] C. E. Nabuco de Araujo, Jr., *Rev. chim. ind.* (*Rio de Janeiro*), 1933, **2**, 187; *Chem. Abs.*, 1934, **28**, 3918. H. F. Hofmann and J. G. Park, U. S. P. 2,006,166, June 25, 1935, to Stanco, Inc.; *Brit. Chem. Abs.* **B**, 1936, 653; *Chem. Abs.*, 1935, **29**, 5681. A discussion of the solvent properties of methyl isobutyl ketone is found in *Paint Var. Prod. Man.*, 1934, 11 (6), 10; *Brit. Chem. Abs.* **B**, 1935, 91.

[191] British P. 430,664, 1935, to Deutsche Hydrierwerke A.-G.; *J. Inst. Pet. Tech.*, 1935, **21**, 344A; *Brit. Chem. Abs.* **B**, 1935, 775.

[192] See Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**.

Chapter 19

Sulphur and Sulphur Compounds in Petroleum and Its Distillates. Their Occurrence, Chemical Properties and Possible Applications

All crude petroleums contain sulphur compounds, though the proportion of such bodies varies widely depending upon the source of the oil.[1] Pennsylvanian and Rumanian oils probably have the smallest amounts, being about 0.03 per cent or less. Some American oils, such as those from fields in Texas, possess about 1 to 2.5 per cent, and the highest sulphur content (about 5 per cent) is generally associated with Mexican crudes. Practically all types of sulphur derivatives have been isolated from mineral oil distillates. Thus, Kazarnovskaya and Sosnina[2] state they found elemental sulphur, hydrogen sulphide, mercaptans, thioethers, disulphides and thiophenes in the gasoline and kerosene fractions of Russian crudes. The presence of amyl mercaptan and *sec*-hexyl mercaptan in the gasoline cut boiling at 113-155°C. (from Japanese shale oil) has been reported,[3] and a lower-boiling (below 40°C.) distillate contained dimethyl sulphide and ethyl mercaptan.[4]

One objection to sulphur or its derivatives in petroleum products is the corrosive action on metals. This may occur when the distillates are stored, or from the sulphur dioxide (and subsequent sulphuric acid) formed when the liquids are employed as fuels in internal combustion engines.[5] There has been considerable controversy as to the maximum, permissible sulphur content of refined oils, particularly for gasoline and kerosene. In spite of the wide differences of opinions on this question, in the United States an almost universal value of 0.1 per cent total sulphur was adopted. In addition the fuel should be non-corrosive to copper, thus indicating the absence or only a very small proportion of elemental sulphur.

The effect of sulphur derivatives on the color stability of gasolines was investigated by Egloff, Morrell, Benedict and Wirth.[6] With straight-run distillates, the addition of ethyl, *n*-propyl or *n*-amyl mercaptans had little effect on the color when the sample was exposed to light from a carbon arc lamp. (See Fig. 119.) When the corresponding disulphides were incorporated, however, the gasoline became cloudy after exposure. In the case of cracked distillates or these blended with straight-run fractions, both types of sulphur compounds effected a development of haze and a deepening in color. The latter phenomena were most marked with elemental sulphur in cracked gasolines. Both haze and color could be removed from straight-run products by filtration through paper, thus indicating that suspended particles were responsible for these effects. Filtration (after exposure) of cracked spirits clarified, but only slightly improved, color, showing that in this instance

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[1] G. Free, *Oel, Kohle, Erdol Teer*, 1936, **12** (15), 311; *Chem. Abs.*, 1936, **30**, 6173; *J. Inst. Pet. Tech.*, 1936, **22**, 299A.

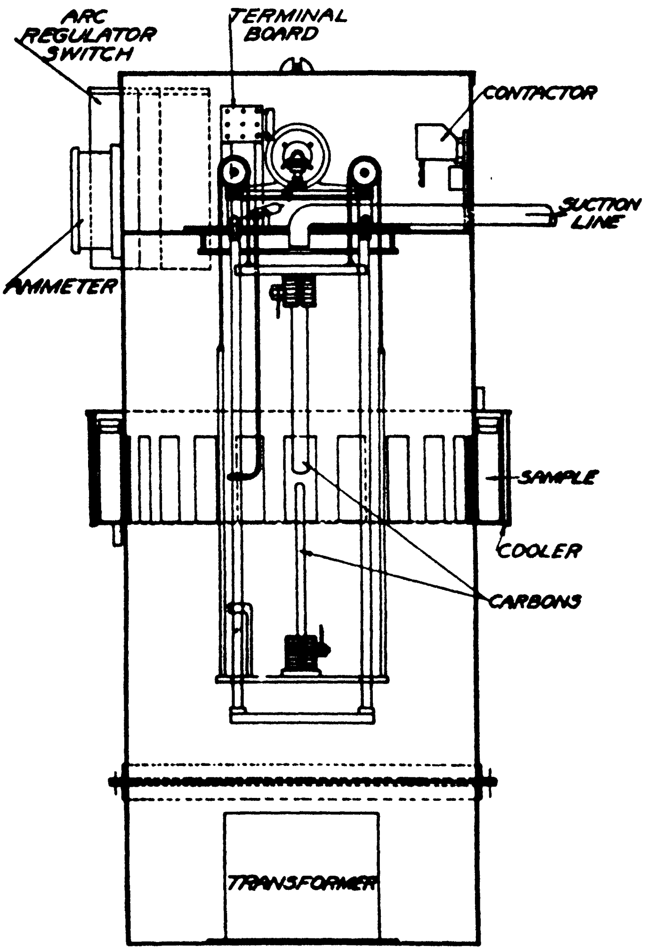
[2] M. A. Kazarnovskaya and A. S. Sosnina, *O.N.T.I. Gorno-Geol.-Neft. Izdat., Crude Oils, Bitumens and Gases from non-Caucasian Deposits*, 1934, 202; *Chem. Abs.*, 1935, **29**, 2707; *Brit. Chem. Abs.* **B**, 1935, 1029. The estimation of various sulphur compounds in distillates from Russian crudes is described by S. M. Gabriel'yantz and O. A. Artem'eva, *Grosnenskii Neftyanik*, 1934, **4** (8), 41; *Chem. Abs.*, 1935, **29**, 2725; *Brit. Chem. Abs.* **B**, 1935, 1029. *Cf.* S. M. Gabriel'yantz and O. Artem'eva, *Novosti Neftepererabotki*, 1936, **3** (11), 7; *Chem. Abs.*, 1936, **30**, 6929.

[3] F. Horie, *J. Soc. Chem. Ind., Japan*, 1936, **39**, Suppl. binding 13; *Chem. Abs.*, 1936, **30**, 3982.

[4] F. Horie, *J. Soc. Chem. Ind., Japan*, 1935, **38**, Suppl. binding 3; *Chem. Abs.*, 1935, **29**, 2708; *Brit. Chem. Abs.* **B**, 1935, 391.

[5] H. R. Ricardo, *J. Inst. Automobile Engrs.* (*London*), 1933, **1** (6), 13; *Chem. Abs.*, 1935, **29**, 587; *Brit. Chem. Abs.* **B**, 1935, 438.

[6] G. Egloff, J. C. Morrell, W. S. Benedict and C. Wirth III, *Ind. Eng. Chem.* 1935, **27**, 323; *J. Inst. Pet. Tech.*, 1935, **21**, 204A; *Brit. Chem. Abs.* **B**, 1935, 535; *Chem. Abs.*, 1935, **29**, 2716.



Courtesy Industrial and Engineering Chemistry

FIG. 119.—Carbon Arc Apparatus for Determining Color Stability of Gasoline. (G. Egloff, J. C. Morrell, W. L. Benedict and C. Wirth, III)

soluble colored compounds had been formed. Substitution of individual hydrocarbons, viz., *n*-heptane, 2,2,4-trimethylpentane, octene-2, diisobutylene, cyclohexene, cyclopentadiene, benzene and toluene for gasolines led to analogous results.[7] In the presence of elemental sulphur all the hydrocarbons developed color on exposure to light, and all reacted with this element. The olefins and cycloolefins furnished hydrogen sulphide and mercaptans, while the paraffins, cycloparaffins and aromatics gave hydrogen sulphide and thioethers. It was also found that on dissolving *n*-propyl disulphide in the hydrocarbons and exposing the solutions to light and oxygen that sulphur dioxide and trioxide were formed. If the tests were carried out in an atmosphere of nitrogen or hydrogen the development of mercaptans was observed.

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[7] J. C. Morrell, W. L. Benedict and G. Egloff, *Ind. Eng. Chem.*, 1936, **28**, 448; *Chem. Abs.*, 1936, **30**, 3979.

Schulze and Buell[8] have shown that organic sulphur compounds reduce the lead susceptibility of motor fuels, i.e., the increase in octane number on the addition of lead tetraethyl is less per unit volume of reagent the greater the proportion of sulphur in the fuel. In general, alkyl disulphides are the most harmful in this respect and thioethers less so, while cyclic compounds exhibit the least effect. Comparison of aliphatic sulphides and disulphides indicated that reduction of octane number was greater with the homologues of higher molecular weights and with the branched-chain isomers. Results obtained with some disulphides are given in Table 102.

TABLE 102.—*Effect of Disulphides on Lead Susceptibility of Gasoline.*

Compound	Wt. % Sulphur Added	Octane Number at cc. of Lead Tetraethyl per Gallon 0	1	2	3	6
Reference fuel	—	51.0	63.5	70.7	74.7	79.5
Methyl disulphide	0.39	48.9	52.4	53.0	56.2	64.5
Ethyl disulphide	0.41	48.4	52.4	55.6	58.2	64.5
n-Butyl disulphide	0.064	50.6	58.7	63.6	66.5	72.7
sec-Butyl disulphide	0.028	50.3	59.6	65.8	69.5	75.8
ter-Butyl disulphide	0.028	50.6	59.6	65.4	69.1	75.6
Benzyl disulphide	0.034	49.3	58.8	64.6	68.6	76.2
Diphenyl disulphide	0.036	49.9	59.6	66.1	69.8	76.6

Schulze and Buell also found that reducing the sulphur content of a natural gasoline from 0.037 to 0.008 per cent increased the octane number by two points. Furthermore, the addition of 1 cc. of lead tetraethyl to the desulphurized fuel yielded a product having an 81 octane number as compared with 75.6 for the untreated gasoline and same quantity of lead.

Because of the above mentioned effects, corrosion, light instability, and change in anti-knock property of fuel, removal of at least part of the sulphur in some types of petroleum distillates is practically imperative. The resulting accumulation of sulphur-containing substances as by-products of refining operations has stimulated efforts towards their utilization. For this reason the chemistry of the various types of sulphur derivatives found in petroleum and their possible applications are of interest.

HYDROGEN SULPHIDE

Because of its well-known highly toxic property and its corrosive action on metals,[9] the elimination of hydrogen sulphide from petroleum distillates and refinery gases, particularly those from high-sulphur crudes, is of importance. In the case of distillates, extraction with solutions of alkalies, such as sodium hydroxide or carbonate, or with aqueous suspensions of less soluble metallic hydroxides, e.g., magnesium hydroxide, is usually sufficient.[10] Crosby and Carney[11] suggest the use of aqueous suspensions of lime, operation being conducted under pressure to prevent the formation of emulsions. In the procedure, the distillate and suspension of lime are admixed in a series of U-tubes (Fig. 120) under a gage pressure of 20-45 lbs. per sq. in. In this manner, hydrogen sulphide is said to be converted to calcium hydrogen sulphide. After a contact period of 1 minute the mixture is conducted to a separator. In the latter three layers are formed, the upper layer consisting of the distillate, the middle of unused lime, and the lower of calcium hydrogen sulphide. The distillate may then be scrubbed with dilute caustic soda to remove the remaining hydrogen sulphide. Unused lime may be recycled, while the calcium hydrogen sulphide is discarded or employed in preparing fresh lime suspension. Vacuum flashing of kerosene, to eliminate 60-90 per cent of dissolved hydrogen sulphide, followed by caustic washing is proposed by Woods.[12] Another method consists in agitating the distillate with a water solution of sulphur dioxide, whereby hydrogen sulphide is oxidized to elemental sulphur.[13] The resulting aqueous suspension of sulphur is then separated and added to a sour distillate, which has been subjected to treatment with sodium plumbite, to effect sweetening (*q.v.*).

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[8] W. A. Schulze and A. E. Buell, *Nat. Pet. News*, 1935, **27** (41), 25; *Chem. Abs.*, 1935, **29**, 8306. *Oil & Gas J.*, 1935, **34** (21), 22; *Chem. Abs.*, 1936, **30**, 838. *Oil & Gas J.*, 1936, **34** (38), 28. See also S. F. Birch and R. Stansfield, *Ind. Eng. Chem.*, 1936, **28**, 668; *Chem. Abs.*, 1936, **30**, 5401; *J. Inst. Pet. Tech.*, 1936, **22**, 307A; *Brit. Chem. Abs.* **B**, 1936, 775.

[9] The corrosion of gas holders is discussed by H. Hollings and W. K. Hutchison, *Chem. & Ind.*, 1935, 726, 752; *Brit. Chem. Abs.* **B**, 1935, 932; *Chem. Abs.*, 1935, **29**, 6733. *Gas World*, 1935, **102**, 676, 696; *Gas. Industry*, 1935, **52**, 317, 417; *Chem. Abs.*, 1935, **29**, 6022. For a description of the effect of sulphur-crudes on pipe-lines, see W. F. Rogers, *Oil & Gas J.*, 1935, **34** (23), 69; *J. Inst. Pet. Tech.*, 1936, **22**, 15A. Prevention of corrosion of distillation equipment by employing aqueous caustic soda is described by L. Sel'skii, *Grosnenskii Neftyanik*, 1934, **4** (8), 45; *Brit. Chem. Abs.* **B**, 1935, 1031; *Chem. Abs.*, 1935, **29**, 2719.

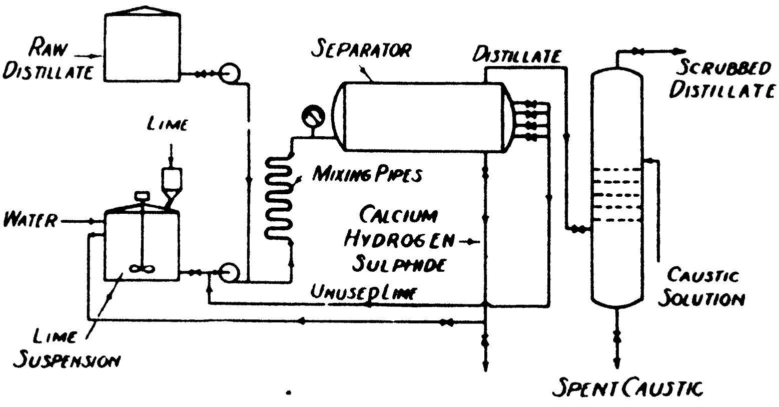

FIG. 120.—Sketch of Method for Removal of Hydrogen Sulphide by Treatment of Petroleum Distillates with Lime Suspensions. (R. H. Crosby and B. R. Carney)

Although hydrogen sulphide may be removed from gaseous mixtures by washing with water[14] (under pressure), aqueous inorganic alkalies are more often employed for this purpose. In the case of sodium carbonate the reaction is

$$Na_2CO_3 + H_2S \longrightarrow NaHS + NaHCO_3$$

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[10] For a review of these methods, see Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, 1934.

[11] R. H. Crosby and B. R. Carney, U. S. P. 2,030,245, Feb. 11, 1936, to Shell Development Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 213A; *Chem. Abs.*, 1936, **30**, 2362.

[12] G. M. Woods, *Petroleum Eng.*, 1936, 7 (5), 84; *J. Inst. Pet. Tech.*, 1936, **22**, 206A; *Chem. Abs.*, 1936, **30**, 3212.

[13] W. G. Hamilton, R. G. Follis and H. P. McCormick, U. S. P. 1,993,140, Mar. 5, 1935, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1935, **29**, 2731; *Brit. Chem. Abs.* B, 1936, 261.

[14] German P. 604,294, 1934, to Metallges. A.-G.; *Chem. Abs.*, 1935, **29**, 914.

Recovery of hydrogen sulphide from the spent liquor may be accomplished by dissolving sufficient carbon dioxide in it until all sodium carbonate is converted to the bicarbonate and subjecting the solution to reduced pressure, heating slightly if necessary.[15] Stronger heating then liberates carbon dioxide and changes sodium bicarbonate to carbonate. Rosenstein and Kramer[16] suggest washing gases with a solution of tripotassium phosphate. Hydrogen sulphide may be regenerated by heating the extraction medium. Various types of organic bases have been recommended also, such as triethanolamine,[17] N-ethylglycocoll and sodium salts of dimethyl-N-anthranilic acid,[18] ethylenediamine, quinoline, pyridine, or their homologues[19] (in organic solvents), or tri- or tetramines,[20] e.g., monohydroxymethyldiethylenetriamine.

If the gases contain both hydrogen sulphide and carbon disulphide and aqueous calcium hydroxide be employed as the extraction medium then calcium thiocarbonate is formed.[21] The reactions occurring in this instance may be indicated in the following manner:

$$Ca(OH)_2 \xrightarrow{H_2S} Ca(SH)_2 \xrightarrow{H_2O} Ca(OH)(SH) \xrightarrow{CS_2} Ca(OH)_2 \cdot CaCS_3$$

Concentrated aqueous solutions of sodium phenolates or sodium salts of tar acids are proposed by Shaw[22] as extraction media. The phenolates from a shale tar (boiling 200-300°C.) are reported to absorb hydrogen sulphide three times as rapidly as carbon dioxide, thus affording a method for the separation of these gases.[23] Another procedure consists in passing the gases through an aqueous suspension of manganese oxide or hydroxide, whereby manganese sulphide is formed and also carbonate, if carbon dioxide be present.[24] Treatment of the mixed manganese compounds with steam results in hydrolysis of the sulphide and liberation of hydrogen sulphide. On heating the residue, out of contact with air, the carbonate is decomposed into manganese oxide and carbon dioxide.

Alkaline solutions of the oxides or salts of arsenic, antimony or tin, have been recommended as extracting agents for hydrogen sulphide.[25] A two-stage process involving partial removal of the sulphide by such solutions and elimination of residual hydrogen sulphide with aqueous ammonium sulphite is described by Eymann.[26] In other instances aqueous suspensions of metallic hydroxides, e.g., those of iron, zinc, or manganese, may be employed in the first stage, and an aqueous solution of a thionate in the second stage.[27] The use of ammonium bisulphite solutions at 60-100°C. has been proposed.[28]

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[15] G. H. Hultman and C. W. Pilo, British P. 436,218, 1935; *Brit. Chem. Abs.* **B**, 1936, 53; *Chem. Abs.*, 1936, **30**, 1982.

[16] L. Rosenstein and G. A. Kramer, U. S. P. 1,945,163, Jan. 30, 1934, to Shell Development Co.; *Brit. Chem. Abs.* **B**, 1935, 227; *Chem. Abs.*, 1934, **28**, 2478. French P. 795,596, 1936 to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 6181.

[17] J. D. Seguy, U. S. P. 1,986,228, Jan. 1, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 1241; *J. Inst. Pet. Tech.*, 1935, **21**, 138A; *Brit. Chem. Abs.* **B**, 1935, 1126 cf. H. Baehr, U. S. P. 2,045,747, June 30, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 5771. British P. 444,327, 1936; *Brit. Chem. Abs.* **B**, 1936, 583.

[18] H. Ulrich, H. Dehnert and F. A. Fries, U. S. P. 2,011,386, Aug. 13, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 6477.

[19] British P. 417,379, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1234; *Brit. Chem. Abs.* **B**, 1935, 55.

[20] H. Baehr and W. Wenzel, German P. 620,932, 1935, to I. G. Farbenind A.-G.; *Chem. Abs.*, 1936, **30**, 1897.

[21] C. P. Dubbs, U. S. P. 1,952,703, Mar. 27, 1934, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1935, 89; *Chem. Abs.*, 1934, **28**, 3577.

[22] J. A. Shaw, U. S. P. 2,028,124, Jan. 14, 1936, to Koppers Co. of Delaware; *Chem. Abs.*, 1936, **30**, 1546. U. S. P. 2,028,125, Jan. 14, 1936; *Chem. Abs.*, 1936, **30**, 1546. See also M. Shoeld, U. S. P. 2,002,257, May 21, 1935, to Koppers Co. of Delaware; *Chem. Abs.*, 1935, **29**, 4554.

[23] A. Dobryanskii, I. Nikhamov, D. Aleksandrovich and V. Tret'yakov, *Goryuchie Slantsui*, 1935, **5** (1), 42; *Chem. Abs.*, 1936, **30**, 3620; *J. Inst. Pet. Tech.*, 1936, **22**, 351A.

[24] K. Koller, Hungarian P. 113,893, 1936; *Chem. Abs.*, 1936, **30**, 3180. For the preparation of the manganese oxide, see M. O. Kharmandar'yan and E. L. Kopeliovich, *J. Applied Chem.* (*U.S.S.R.*), 1936, **9**, 23; *Chem. Abs.*, 1936, **30**, 6141.

[25] M. V. Hoftman, S. G. Aronov and E. M. Mikhel'son, *Coke and Chem.* (*U.S.S.R.*), **1933**, No. 5, 49; *Chem. Abs.*, 1935, **29**, 3140; *Brit. Chem. Abs.* **B**, 1936, 6. M. V. Hoftman, S. G. Aronov, S. E. Senitchenko, *Coke and Chem.* (*U.S.S.R.*), **1936**, No. 2-3, 91; *Brit. Chem. Abs.* **B**, 1936, 965. H. A. Gollmar, U. S. P. 1,957,262, May 1, 1934, to Koppers Co. of Del.; *Chem. Abs.*, 1934, **28**, 4211; *Brit. Chem. Abs.* **B**, 1935, 294. German P. 611,618, 1935, to Heinrich Koppers G.m.b.H.; *Chem. Abs.*, 1935, **29**, 6027; *J. Inst. Pet. Tech.*, 1935, **21**, 266A. Heinrich Koppers G.m.b.H., British P. 443,407, 1936, to Heinrich Koppers' Industrieele Maatschappij N. V.; *J. Inst. Pet. Tech.*, 1936, **22**, 199A; *Brit. Chem. Abs.* **B**, 1936, 485; *Chem. Abs.*, 1936, **30**, 5398. A. R. Powell, *Chem. Met. Eng.*, 1936, **43**, 307; *Chem. Abs.*, 1936, **30**, 5764. *Gas Age*, 1936, **77** (26), 711. *Gas J.* 1936, **215**, 277; *Chem. Abs.*, 1936, **30**, 6924. Operations involving the use of such solutions are known as

Other processes comprise treatment with ammonia or sulphur dioxide in the gaseous phase[29] or with sulphur dioxide dissolved in an organic base such as pyridine or quinoline.[30] Or the gases containing hydrogen sulphide are scrubbed with an aqueous solution containing two or more electrolytes,[31] e.g., sodium chloride and magnesium sulphate, or phosphoric acid and ammonium sulphate, after which the liquids are treated with gases made by burning sulphur.[32] Also it has been reported that hydrogen sulphide may be removed from crude gasoline by lowering

FIG. 121.
View of Gas-purification Plant Employing Thioarsenates for Removal of Hydrogen Sulphide. Thylox Process. (H. A. Gollmar)

Courtesy Koppers Company
Courtesy Industrial and Engineering Chemistry

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the "Thylox" process. See H. A. Gollmar, *Ind. Eng. Chem.*, 1934, **26**, 130; *Chem. Abs.*, 1934, **28**, 1841; *J. Inst. Pet. Tech.*, 1934, **20**, 181A, *Brit. Chem. Abs.* **B**, 1934, 485.

[26] C. Eymann, U. S. P. 2,002,365, May 21, 1935, to Koppers Co. of Delaware; *Chem. Abs.*, 1935, **29**, 4554; *Brit. Chem. Abs.* **B**, 1936, 583.

[27] C. Eymann, U. S. P. 1,975,253, May 1, 1934, to Koppers Co. of Delaware; *Brit. Chem. Abs.* **B**, 1935, 88.

[28] A. G. Rembashevskii and V. V. Morozov, Russian P. 40,496, 1934; *Chem. Abs.*, 1936, **30**, 3974.

[29] P. E. Kuhl, U. S. P. 2,028,336, Jan. 21, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 1546 For the use of anhydrous ammonia in the neutralization of acidic liquids or vapors in petroleum distillation equipment, see R. E. Woodward, *Oil & Gas J.*, 1934, **33** (17), 33; *J. Inst. Pet. Tech.*, 1935, **21**, 20A; *Chem. Abs.*, 1934, **28**, 7497.

[30] British P. 430,865, 1935, to C. Otto & Co. G.m.b.H.; *Chem. Abs.*, 1935 **29**, 8257; *J. Inst. Pet. Tech.*, 1935, **21**, 343A; *Brit. Chem. Abs.* **B**, 1935, 891. French P. 776,063, 1935; *Chem. Abs.*, 1935, **29**, 3473.

[31] Employment of organic salts in non-aqueous liquids has also been suggested. *Cf.* W. K. Hutchison and G. Dougill, British P. 456,661, 1936, to Gas Light & Coke Co.; *Brit. Chem. Abs.* **B**, 1937, 14; *J. Inst. Pet. Tech.*, 1937, **23**, 56A; *Chem. Abs.*, 1937, **31**, 3245.

[32] M. J. Leahy, U. S. P. 1,995,545, Mar. 26, 1935; *Brit. Chem. Abs.* **B**, 1936, 437; *Chem. Abs.*, 1935, **29**, 3143. *Refiner*, 1936, **15**, 276; *J. Inst. Pet. Tech.*, 1936, **22**, 439A.

the pressure over the latter.[33] In this manner the sulphide is said to be separated together with some of the lower boiling hydrocarbons. Rectification of the gaseous portion is then effected to recover the hydrocarbon present. The use of muddy iron ore has been suggested in another method.[34] Chlorine may also be employed to replace the sulphur in hydrogen sulphide.[35] The sulphur is then treated at 112-170°C. with hydrogen sulphide. Pure sulphur is said to be furnished in this way.

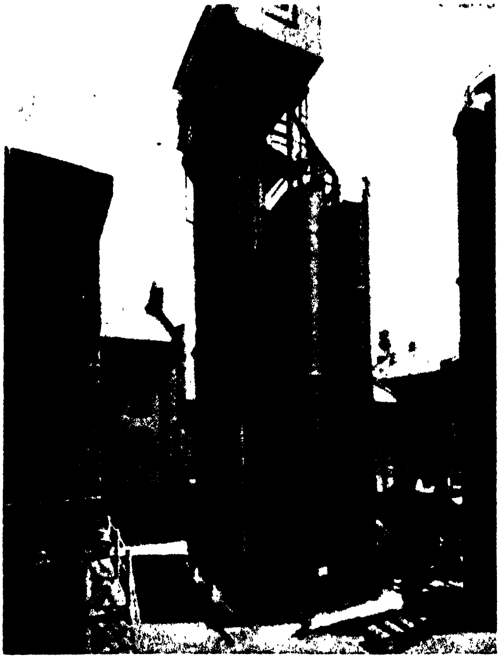

FIG. 122.
View of Thylox Gas-purification Plant. (H. A. Gollmar)

Courtesy Koppers Company
Courtesy Industrial and Engineering Chemistry

CATALYTIC OXIDATION OF HYDROGEN SULPHIDE

The ease with which hydrogen sulphide is oxidized to water and elemental sulphur furnishes a basis for the removal of this compound from either liquid or gaseous mixtures. For example, aqueous liquids used in scrubbing gases are caused to flow simultaneously with a stream of air (or oxygen) over coke or pumice on which a catalyst is supported.[36] The latter may consist of metallic hydroxides or oxides, such as those of titanium, vanadium, chromium, iron, molybdenum or tungsten. When water contains dissolved or suspended low-boiling organic compounds, e.g., benzene, it can be conducted through two filters of activated carbon, the first of which adsorbs sulphur or sulphur compounds, and the second the organic substances.[37] The liquid is treated with oxygen (or other oxidizing agents) before passage through the first filter.

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[33] M. P. Youker, U. S. P. 2,048,241, July 21, 1936, to Phillips Petroleum Co.; *Chem. Abs.*, 1936, **30**, 6184; *J. Inst. Pet. Tech.*, 1936, **22**, 453A.

[34] French P. 799,536, 1936, to Soc. Aug. Klönne; *Chem. Abs.*, 1936, **30**, 7796.

[35] W. Schornstein and J. Theberath, German P. 630,325, 1936; *Chem. Abs.*, 1936, **30**, 5739.

[36] H. Hollings and W. K. Hutchison, British P. 421,643, 1934, to The Gas Light & Coke Co.; *Chem. Abs.*, 1935, **29**, 3814. *Cf.* G. V. Petrov, *Coke and Chem.* (*U.S.S.R.*), **1936**, No. 2-3, 67; *Brit. Chem. Abs.* **B**, 1936, 965.

[37] German P. 623,479, 1935, to Carbo-Norit-Union Verwaltungs-Ges.m.b.H.; *Chem. Abs.*, 1936, **30**, 2054.

Preferential oxidation of hydrogen sulphide in producer gas[38] or in gases from hydrogenation or cracking operations[39] may be effected in the presence of activated carbon. Aqueous ammonium sulphide is employed for extraction of elemental sulphur from the catalyst and reactivation of the latter carried out at 110-120°C.[40] Kazarnovskii and Pisarev[41] suggest adding oxygen to the extent of 25 per cent excess over that required for oxidation of hydrogen sulphide, 3 per cent ammonia, and then heating the mixture to 70-75°C. Afterwards the gaseous mixture is conducted over carbon at 115-120°C. It is reported that iodine-treated activated charcoal has a greater adsorptive power for hydrogen sulphide (and also sulphur dioxide) than pure activated charcoal.[42]

A process developed by Bacon[43] includes bringing gases, containing hydrogen sulphide as an impurity, into contact with alkaline solutions in the presence of oxygen. A mixture of zinc or iron salts may be added as catalyst to the alkali and operation conducted under pressure.

PROPERTIES OF HYDROGEN SULPHIDE

Under atmospheric pressure and ordinary temperatures, hydrogen sulphide is a gas. It can be condensed to a liquid boiling at —59.6°C. and freezing at —82.9°C. The critical temperature and pressure of this sulphide are 100.4°C. and 88.9 atmospheres, respectively.[44] The density of the liquid at temperatures ranging from —81° to 58°C. was determined by Baxter, Burrage and Tanner,[45] who found the value at the lower temperature was 0.938 and 0.680 at the higher temperature. The results of these investigators are shown graphically in Fig. 123. The solubility of hydrogen sulphide in hydrocarbons, e.g., hexane, benzene, or toluene, is generally greater than in water. The distribution coefficients,[46] at various temperatures, of this sulphide between benzene and water are given in Table 103.

TABLE 103.—*Distribution Coefficients of Hydrogen Sulphide between Benzene and Water.*

Temperature, °C.	Distribution Coefficient
6	5.3
12	5.55
20	5.7
30	5.75
40	5.81

The solubility of different types of hydrocarbons in liquid hydrogen sulphide was investigated by Terres and Vollmer.[47] They noted that at 0°C. paraffins, aromatics (such as benzene and toluene), hydroaromatics and heterocyclic compounds (e.g., quinoline) were miscible in all proportions. Other compounds, for example, phenol, *o*-cresol and dicyclic hydrocarbons (naphthalene) exhibited a high solubility in the liquid. All the substances investigated formed only one liquid phase with hydrogen sulphide and in no case was a miscibility gap observed. Toluene, phenol and quinoline formed intermediate compounds of the types, $2C_6H_5CH_3 \cdot H_2S$, $2C_6H_5OH \cdot H_2S$ and $C_9H_7N \cdot H_2S$, respectively. Octadecane and hexahydrobenzene yielded solid solutions with hydrogen sulphide.

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[38] P. Herold and W. Baumann, U. S. P. 1,984,971, Dec. 18, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1234. French P. 796,294, 1936; *Chem. Abs.*, 1936, **30**, 6146.

[39] K. Götze, German P. 615,510, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 8297

[40] A. Tyulyukov and M. Khrenova, *J. Chem. Ind. (Moscow)*, 1935, **12**, 247; *Chem. Abs.*, 1935, **29**, 4921; *Brit. Chem. Abs.* **B**, 1935, 708.

[41] S. Kazarnovskii and K. Pisarev, *J. Chem. Ind. (Moscow)*, 1935, **12**, 913; *Chem. Abs.*, 1936, **30**, 823; *Brit. Chem. Abs.* **B**, 1936, 177.

[42] V. A. P'yankov, *J. Gen. Chem. (U.S.S.R.)*, 1935, **5**, 1112; *Chem. Abs.*, 1936, **30**, 927.

[43] T. S. Bacon, U. S. P. 2,019,468, Oct. 29, 1935, to Lone Star Gas Co.; *Chem. Abs.*, 1936, **30**, 272.

[44] These values are from "International Critical Tables," McGraw-Hill Book Co., New York, **1928**. For a discussion of the transformations of solid hydrogen sulphide, see E. Justi and H. Nitka, *Physik. Z.*, 1936, **37**, 435; *Brit. Chem. Abs.* **A**, 1936, 926; *Chem. Abs.*, 1936, **30**, 5853.

[45] J. P. Baxter, L. J. Burrage and C. C. Tanner, *J.S.C.I.*, 1934, **53**, 410T. *Chem. Abs.*, 1935, **29**, 3890; *Brit. Chem. Abs.* **A**, 1935, 290.

[46] S. A. Shchukarev and I. B. Khakham, *J. Gen. Chem. (U.S.S.R.)*, 1935, **5**, 1056; *Chem. Abs.*, 1936, **30**, 2464.

[47] E. Terres and W. Vollmer, *Petroleum Z.*, 1935, **31** (19), 1; *Chem. Abs.*, 1935, **29**, 8302; *Brit. Chem. Abs.* **B**, 1935, 581; *J. Inst. Pet. Tech.*, 1935, **21**, 251A.

Miscellaneous Reactions of Hydrogen Sulphide. Combination of olefins and hydrogen sulphide at high temperatures (650-725°C.) in the presence of catalysts furnishes a variety of products, including mercaptans, thiophene and its homologues, thioethers and carbon disulphide. At lower temperatures (200-300°C.) mainly mercaptans are formed.[48] Propene and hydrogen sulphide, according to Barr and Keyes,[49] reacted, when using a nickel sulphide catalyst, to yield isopropyl and *n*-propyl mercaptans in the ratio of approximately 2:1. The temperature range was 200-300°C., and larger yields were obtained at the lower temperatures. Some of the results of these investigators are given in Table 104.

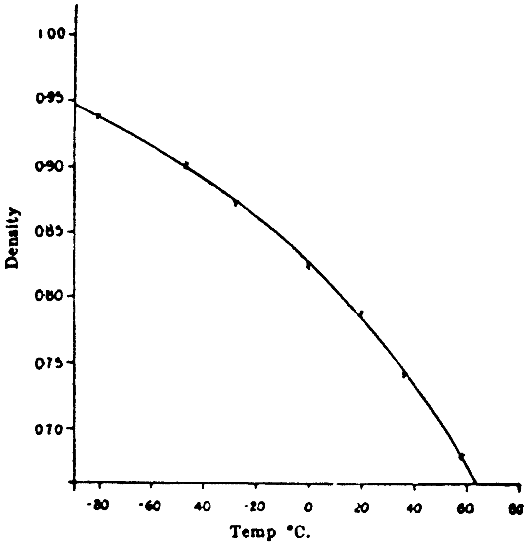

FIG. 123.
Temperature-Density Curve for Liquid Hydrogen Sulphide. (J. P. Baxter, L. J. Burrage and C. C. Tanner)

Courtesy Journal of Society of Chemical Industry

TABLE 104.—*Yields of Mercaptans from Propene and Hydrogen Sulphide.*

Temp. °C.	Total Mercaptan Conversion %	Isopropyl Mercaptan %	*n*-Propyl Mercaptan %
300	12	7.8	4.2
275	19	12.3	6.7
250	29	18.8	10.2
225*	40	26.0	14.0
200*	50	32.5	17.5

* Figures at these temperatures are estimated.

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[48] For review of these methods, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[49] F. T. Barr and D. B. Keyes, *Ind. Eng. Chem.*, 1934, **26**, 1111; *Chem. Abs.*, 1934, **28**, 7124; *Brit. Chem. Abs.* **A**, 1934, 1307. cf. C. C. Allen, U. S. P. 2,051,806, Aug. 25, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 6764. E. C. Williams and C. C. Allen, U. S. P. 2,052,268, Aug. 25, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 7122

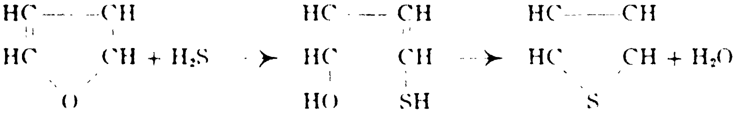
Union of hydrogen sulphide and isobutene may be effected in the following manner:[50] The olefin is dissolved in cold 75-80 per cent sulphuric acid, yielding a mixture of *ter*-butyl acid sulphate and di-*ter*-butyl sulphate. A rapid stream of hydrogen sulphide is passed into these sulphates whereupon an oily layer of mercaptans is formed. After completion of the reaction and dilution of the mixture with water, the upper layer is removed, washed with water, dried and distilled. It consists essentially of *ter*-butyl mercaptan.

Analysis indicated that a mixture of 2-thiol-2-methylbutene-3 and 2,3-dithiol-2-methylbutane

$$(CH_3)_2C(SH)CH{=}CH_2 \quad \text{and} \quad (CH_3)_2C(SH)CH(SH)CH_3$$

respectively, resulted from the action of hydrogen sulphide on isoprene at 96°C., using ferric oxide as a catalyst.[51] The former compound was readily oxidized by peracetic acid. Further investigation was precluded by the odor of the products.

Nenitzescu and Scarlatescu[52] report that passage of gaseous hydrogen sulphide and ethylene oxide through a Raschig column results in the formation of β,β'-dihydroxyethyl sulphide, provided the rings have been moistened previously with some of the product. Otherwise reaction does not appear to take place. With furan (another cyclic oxide), at 450°C. and aluminum oxide as a catalyst, substitution of oxygen by sulphur occurs and thiophene is formed.[53] It is suggested in this instance that splitting of the ring takes place with the production of an intermediate hydroxy mercaptan which then undergoes dehydration and cyclization.



Another example of the replacement of oxygen by sulphur (accompanied by ring-formation) is the preparation of *sym*-trithiane from formaldehyde and hydrogen sulphide.[54]

Decomposition of hydrogen sulphide (at −15° to 18°C.) in a high frequency discharge is apparently a first order reaction, proceeding according to the equation

$$dc/dt = K(A - C)$$

in which K is a measure of the speed and A is the limiting concentration of hydrogen sulphide.[55] The values of A and K at various temperatures are:

Temp. °C.	Values of: A	K
18	14 0	3 750
4	57 3	1 034
− 5	73	0 961
−15	86 0	0 250

Polysulphides are probably formed as intermediate products and the rate at which they further disintegrate (wall-reaction) into various sulphur polymers determines the constant K.

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[50] W. M. Lee, U. S. P. 2,020,421, Nov. 12, 1935, *Chem. Abs.* 1936, **30**, 489

[51] J. Boeseken and N. v. d. Linde, *Rec. trav. chim.*, 1935, **54**, 739, *Chem. Abs.*, 1936, **30**, 2912, *Brit. Chem. Abs.* **A**, 1935, 1480

[52] C. D. Nenitzescu and N. Scarlatescu, *Ber.*, 1935, **68**, 587, *Brit. Chem. Abs.* **A**, 1935, 729, *Chem. Abs.*, 1935, **29**, 3979.

[53] Yu. K. Yur'ev, *Ber.*, 1936, **69**, 440; *Chem. Abs.* 1936, **30**, 3815

[54] R. W. Bost and E. W. Constable, "Organic Syntheses" John Wiley & Sons, New York 1936, **16**, 81; *Chem. Abs.*, 1936, **30**, 3825.

[55] L. Kolodkina, *J. Phys. Chem.* (*U.S.S.R.*), 1935, **6**, 428; *Chem. Abs.*, 1936, **30**, 2084

UTILIZATION OF HYDROGEN SULPHIDE

This gaseous sulphide is said to be a cheap and economical raw material for the manufacture of sulphuric acid, yields of the latter as high as 98 per cent having been reported.[55a] The gas is burned with excess air to give water and sulphur dioxide. The latter, mixed with air or oxygen, is converted into sulphur trioxide by passage over a vanadium oxide or tin dioxide and chromium oxide catalyst at 350-400°C. Absorption of the trioxide in water yields sulphuric acid. A flow diagram of one such method is indicated in Fig. 124. This process is applicable to mixed gases containing hydrogen sulphide, such as those from coke ovens or hydrogenation operations.

When mixed with inert gases, complete conversion of the sulphide into sulphuric acid is not economically feasible.[56] For instance, with a gas whose composition is 30 per cent hydrogen sulphide and 70 per cent carbon dioxide only 70 per cent removal of the former (as sulphuric acid) is considered practicable.

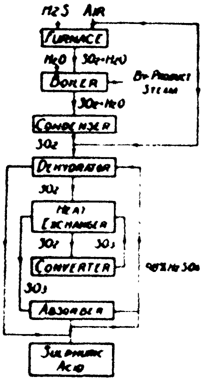

FIG. 124.
Flow Diagram for Manufacture of Sulphuric Acid from Hydrogen Sulphide. (I. Hechenbleikner, T. C. Oliver and S. F. Spangler)

Another method of utilization comprises treatment with halogens (chlorine or bromine) in the presence of sulphur mono- or dichloride.[57] The hydrogen halide thus formed is afterwards washed with a hydrocarbon, e.g., xylene. Drosdoff and Truog[58] suggest stripping iron oxide coatings from minerals by suspending the sample in water, treating with hydrogen sulphide, and then with 0.05N hydrochloric acid. The ripening of alkali-cellulose by air or a gas containing oxygen is said to be accelerated by the presence of an alkali sulphide, e.g., sodium sulphide.[59]

Mild oxidation of hydrogen sulphide, particularly in the form of its alkali salts, gives rise to thiosulphates. Aqueous solutions of these alkali salts may be obtained by the methods previously described for the purification of gaseous mixtures or of liquids. For example, in the Koppers process in which gases are scrubbed with sodium carbonate solution (for hydrogen sulphide removal) and the latter regenerated by aeration with air (or other oxidizing gases) some thiosulphate is formed.[60] After sufficient accumulation of this compound has taken place it may be recovered from the spent alkali. According to Hasenbach,[61] passage of hydrogen sulphide over sodium sulphide at 300°C. yields sodium hydrosulphide. Treatment of the latter with air at 100-150°C. gives sodium thiosulphate.

[55a] W. Siecke, *Chem. Fabrik*, **1935**, 415; *Chem. Abs.*, 1936, **30**, 577; *Brit. Chem. Abs.* **B**, 1935, 1140. *Metallges. Periodic Rev.*, **1936**, No. 11, 14; *Brit. Chem. Abs.* **B**, 1936, 367. See also *Chem. Trade J.*, 1935, **97**, 391; *J. Inst. Pet. Tech.*, 1936, **22**, 19A. *Ind. Chemist*, 1936, **12**, 167; *Brit. Chem. Abs.* **B**, 1936, 493. W. Siecke and C. ten D. Koolman, German P. 610,448, 1935, to Metallges. A.-G.; *Chem. Abs.*, 1935, **29**, 3788. I. Hechenbleikner, T. C. Oliver and S. F. Spangler, U. S. P. 2,003,442, June 4, 1935, to Chemical Construction Corp.; *Chem. Abs.*, 1935, **29**, 4906; *Brit. Chem. Abs.* **B**, 1936, 833. H. Weittenhiller, *Glückauf*, 1936, **72**, 399; *Chem. Abs.*, 1936, **30**, 6139; *Brit. Chem. Abs.* **B**, 1936, 625.

[56] Hoelzer, *Gas u. Wasserfach*, 1935, **78**, 894; *Chem. Abs.*, 1936, **30**, 1210.

[57] A. M. Clifford, U. S. P. 2,028,087, Jan. 14, 1936, to Wingfoot Corp.; *Chem. Abs.*, 1936, **30**, 1525.

[58] M. Drosdoff and E. Truog, *Am. Mineral*, 1935, 20, 669; *Brit. Chem. Abs.* **A**, 1936, 49; *Chem. Abs.*, 1936, **30**, 5907.

[59] British P. 419,585, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1935, 96; *Chem. Abs.*, 1935, **29**, 3156.

$$2NaHS + 2O_2 \longrightarrow Na_2S_2O_3 + H_2O$$

Meschorer[62] recommends the use of manganese dioxide in the oxidation of aqueous sodium sulphide. This procedure, however, furnishes large proportions of sodium hydroxide and carbonate as by-products. Larger yields of thiosulphate are obtained by air-blowing concentrated sodium sulphide solutions (61 per cent) and employing finely divided activated charcoal as the catalyst.[63] In this instance reaction is vigorous and good temperature control is necessary. Separation of any carbonate and hydroxide may be effected by recrystallization of the thiosulphate and extraction with alcohol.

In place of oxygen, sulphur dioxide (or sulphurous acid or its salts) may be used as the oxidizing agent. For example, aqueous sodium sulphide and sulphur dioxide are conducted simultaneously into a solution of sodium sulphite maintained at 60°C.[64] The delivery rates of the reactants are such that sulphur dioxide is always slightly in excess and neither hydrogen sulphide nor sulphur is formed.

$$2Na_2S + 3SO_2 + Na_2SO_3 \longrightarrow 3Na_2S_2O_3$$

Sodium bisulphite may be used instead of the sulphite.[64a] Or the gas containing

$$2Na_2S + 2NaHSO_3 + 2SO_2 \longrightarrow 3Na_2S_2O_3 + H_2O$$

hydrogen sulphide can be treated with a solution of sodium sulphite and bisulphite at 70-75°C.[65]

$$2Na_2SO_3 + 2NaHSO_3 + 2H_2S \longrightarrow 3Na_2S_2O_3 + 3H_2O$$

Another variation comprises reacting sodium polysulphide with sodium bisulphite at 60°C.[65a]

$$2Na_2S_2 + 6NaHSO_3 \longrightarrow 5Na_2S_2O_3 + 3H_2O$$

Foerster and Mommsen[66] have shown that a large yield of thiosulphate is easily obtained on mixing aqueous sodium hydrogen sulphide and bisulphite in the molecular ratios of 2:1. Also sodium sulphide and sulphur dioxide

$$2NaHS + 4NaHSO_3 \longrightarrow Na_2S_2O_3 + 3H_2O$$

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[60] F. W. Sperr, Jr. and D. L. Jacobson, U. S. P. 1,639,905, Aug 27, 1927, to Koppers Co.; *Brit. Chem. Abs.* **B**, 1927, 815; *Chem. Abs.*, 1927, **21**, 3255. British P. 209,169, 1922; *J.S.C.I.*, 1924, **43**, 164B.

[61] W. Hasenbach, U. S. P. 903,135 and 903,136, Nov. 3, 1908; *J.S.C.I.*, 1908, **27**, 1153; *Chem. Abs.*, 1909, **3**, 694 and 695. See also British P. 23,217B and 23,217C, 1907 to Verein Chem Fabrik; *J.S.C.I.*, 1908, **27**, 282; *Chem. Abs.*, 1909, **3**, 362. German P. 194,881, 1907; *Chem. Zentr.*, 1908, **1**, 910; *Chem. Abs.*, 1908, **2**, 1768.

[62] I. Meschorer, German P. 211,882, 1908; *Chem. Zentr.*, 1909, **2**, 392; *Chem. Abs.*, 1909, **3**, 493.

[63] E. E. Naef, British P. 174,653, 1920; *J.S.C.I.*, 1922, **41**, 215A; *Chem. Abs.*, 1922, **16**, 1835.

[64] H. Howard, U. S. P. 1,760,137, May 27, 1930, to Grasselli Chemical Co.; *Brit. Chem. Abs.* **B**, 1930, 1150; *Chem. Abs.*, 1930, **24**, 3613.

[64a] E. C. Marburg, German P. 380,756, 1921, to Chem. Fabr. Griesheim-Elektron; *J.S.C.I.*, 1924, **43**, 16B.

[65] German P. 527,956, 1930, to I. G. Farbenind. A.-G.; *Chem. Zentr.*, 1931, **2**, 1734.

[65a] German P. 208,633, 1908, to Destrée & Cie.; *J.S.C.I.*, 1909, **28**, 473; *Chem. Abs.*, 1909, **3**, 2042. *Cf.* F. Rüsberg, German P. 370,593, 1919, to Rhenania Verein. Chem. Fabr. A.-G.; *J.S.C.I.*, 1923, **42**, 499A.

[66] F. Foerster and E. Th. Mommsen, *Ber.*, 1924, **57**, 258; *Chem. Abs.*, 1924, **18**, 1254; *J.S.C.I.* 1924, **43**, 253B.

or sodium sulphite and hydrogen sulphide furnish sodium thiosulphate provided the acidity of the reaction mixtures is controlled. This can be done by adding initially sufficient alkali hydroxide to secure formation of sodium bisulphite or hydrosulphide, as required. It is interesting to note that an ore flotation agent may be secured by the interaction of rosin and hydrogen sulphide at 80°C. in the absence of conditions which would promote oxidation.[66a]

DETECTION OF HYDROGEN SULPHIDE

Tests for this compound depend upon its color reaction with reagents, particularly metallic salts. One type of detector consists of filter paper moistened with a solution of lead acetate (10 g.) in 50 per cent aqueous glycerol (100 cc.)[66b] The stain obtained when this treated paper is exposed to the gaseaus sample is reported to be sensitive to 1 part of hydrogen sulphide in 80,000 parts of gas. Another type is essentially a glass tube packed with granules of activated aluminum oxide coated with silver cyanide or lead acetate.[67] Gas is conducted through the tube and the distance over which a color change occurs is a measure of the proportion of hydrogen sulphide. This detector operates at temperatures of —22° to +25°C. and with samples containing 0.0025-0.05 per cent hydrogen sulphide. In another procedure the hydrogen sulphide is absorbed in aqueous silver nitrate, containing 1 per cent of the silver salt.[68] Silver sulphide is precipitated, and dissolved in potassium cyanide solution. On treating the latter with sodium plumbite, colloidal lead sulphide is formed, and its color compared with standard solutions. Bell and Hall[69] recommend a dilute aqueous solution of sodium nitroprusside. In this instance the color changes to pink, mauve, or deep violet depending upon the quantity of sulphide which passes through it.

Landgraf[70] suggests pellets of manganese dioxide coated with sirupy phosphoric acid as an absorption medium in gas analysis. A method for determining the rate of absorption of hydrogen sulphide, as well as the total amount, by gas-purifying materials is described by Brückner.[71] One-half to one gram of the material to be tested is placed in a 500 cc. reaction flask, and then a measured volume of hydrogen sulphide is introduced. The container is kept at 20°C. and the decrease in pressure with time is recorded. Afterwards the sulphur content of the spent absorption agent is determined by treatment with sodium sulphite which is converted to thiosulphate.

ELEMENTAL SULPHUR

The presence of elemental sulphur in petroleum distillates may be attributed to decomposition of complex sulphur compounds during distillation operations, oxidation of dissolved hydrogen sulphide, or employment of an excess of this element in doctor sweetening (*q.v.*). Probably the chief objection to it in low-boiling distillates (gasoline and kerosene) is its corrosive action on metals. A number of

[66a] J. N. Borglin and E. Ott, U. S. P. 2,052,210, Aug. 25, 1936, to Hercules Powder Co.; *Chem. Abs.*, 1936, **30**, 7089.

[66b] P. Woog, R. Sigwalt and J. de Saint-Mars, *Bull. soc. chim.*, 1935, **2** (5), 1214; *Chem. Abs.*, 1935, **29**, 6531; *Brit. Chem. Abs.* **B**, 1935, 948. See also, R. Kraus, *Chem. Fabrik.*, **1936**, 241; *Brit. Chem. Abs.* **A**, 1936, 811; *Chem. Abs.*, 1936, **30**, 4726.

[67] J. B. Littlefield, W. P. Yant and L. B. Berger, *Bur. Mines, Rept. of Investigations*, 3276, **1935**; *Brit. Chem. Abs.* **B**, 1935, 947; *Chem. Abs.*, 1935, **29**, 5382; *J. Inst. Pet. Tech.*, 1935, **21**, 446A.

[68] A. Giberton, *Compt. rend.*, 1933, **197**, 646; *Chem. Abs.*, 1934, **28**, 72. I. S. Shereshevskaya, *J. Applied Chem. (U.S.S.R.)*, 1936, **9**, 572; *Chem. Abs.*, 1936, **30**, 7489; *Brit. Chem. Abs.* **A**, 1936, 811.

[69] J. Bell and W. K. Hall, *Chem. and Ind.*, **1936**, 89; *Chem. Abs.*, 1936, **30**, 2875.

[70] A. Landgraf, *Chem. Fabr.*, **1935**, 71; *Chem. Abs.*, 1935, **29**, 2693; *Brit. Chem. Abs.* **B**, 1935, 390.

[71] H. Brückner, *Brennstoff-Chem.*, 1936, **17**, 21; *Brit. Chem. Abs.* **B**, 1936, 306; *Chem. Abs.*, 1936, **30**, 5764.

procedures, involving the use of alkalies, solid alkali sulphides, and metallic elements (sodium or nickel), have been suggested for its removal from petroleum fractions.[72] This element (sulphur) can be extracted also with aqueous solutions of alkali polysulphides, provided the composition of the latter contains less sulphur than that corresponding to the tetrasulphide.[73]

Reaction of petroleum hydrocarbons with sulphur gives rise to a variety of products. In many instances heterocyclic compounds, e.g., thiophene, are obtained when unsaturated hydrocarbons are employed. For example, acetylene and sulphur at 290-390°C. yield not only thiophene but also thiophenol, carbon disulphide and hydrogen sulphide.[74] According to Hessle,[75] substitution of cracked distillates for acetylene and use of lower temperatures (200-250°C.) results in thiophene derivatives. Oxides or hydroxides of iron, nickel, cobalt, manganese, chromium or the alkali earth metals may be used as contact agents. The reaction products may be separated by fractional distillation and sulphonation of these is reported to furnish materials which can be employed in therapeutic and cosmetic preparations. Distillation of higher-boiling fractions, e.g., asphalt oil, mixed with sulphur until the loss in weight is 22-25 per cent, yields ingredients applicable in coating compositions.[76]

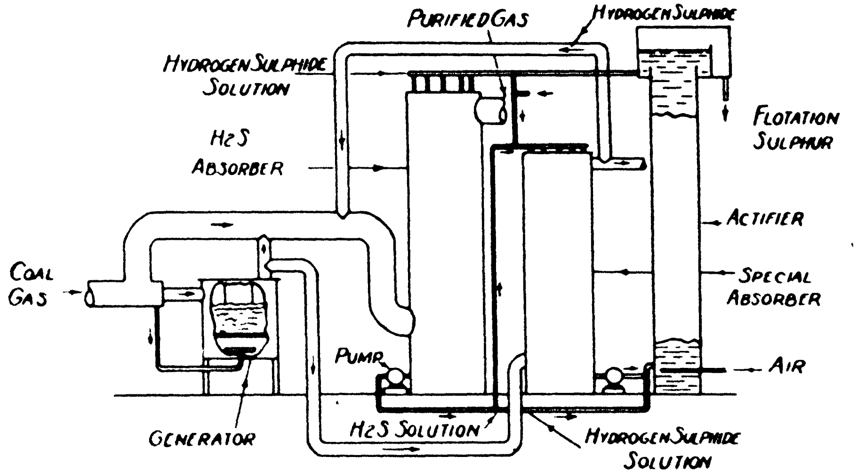

FIG. 125—Sketch of Apparatus for Making Colloidal Sulphur from Hydrogen Sulphide. (C. J. Ramsburg)

Heating sulphur with a hydrocarbon oil or in a current of coal gas and absorption of the resulting hydrogen sulphide by ferric oxides or an aqueous solution of sodium hydroxide followed by treatment with an oxygen-containing gas furnishes colloidal sulphur.[77] The latter may be withdrawn as a froth (Fig. 125) while the partially fouled solution of ferric oxides containing some hydrogen sulphide is employed as an absorption agent for further quantities of the sulphides. Complete conversion of mineral oil (at 400-700°C.) to hydrogen sulphide and carbon disulphide is said to be attained if the heating operation is carried out in a cast iron retort packed with aluminum or stainless steel turnings.[78]

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[72] A discussion of the reactions of elemental sulphur with various compounds is given by Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, **1934**.

[73] W. A. Schulze and L. V. Chaney, U. S. P. 2,020,661, Nov. 12, 1935, to Phillips Petroleum Co.; *Chem. Abs.*, 1936, **30**, 603; *J. Inst. Pet. Tech.*, 1936, **22**, 23A; *Brit. Chem. Abs.* **B**, 1936, 777. See also, A. S. Krendel and V. A. Kitaitzev, *Keram. i Steklo*, 1936, **12** (3), 6; *Chem. Abs.*, 1936, **30**, 5764.

[74] C. T. Bhatt, K. S. Nargund, D. D. Kanga and M. S. Shah, *J. Univ. Bombay*, 1934, **3** (2), 159; *Brit. Chem. Abs.* **B**, 1935, 325; *Chem. Abs.*, 1935, **29**, 4762.

[75] E. T. Hessle, U. S. P. 1,996,334, Apr. 2, 1935, to Thiophene Products Co.; *Brit. Chem. Abs.* **B**, 1936, 444; *Chem. Abs.*, 1935, **29**, 3468.

[76] H. S. Holt, U. S. P. 2,002,634, May 28, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1936, 510; *Chem. Abs.*, 1935, **29**, 4485.

Combination of olefins and sulphur may be effected by submitting the hydrocarbon to the simultaneous action of hydrogen sulphide and the element.[79] Basic substances, such as ammonia, amines, piperidine and substituted guanidines or thiuram sulphides, can be used as carriers for sulphur. Particular applications of this procedure are the vulcanization of rubber or the preparation of factice.

An investigation of the reaction between sulphur and benzene, at 80°C., in the presence of aluminum chloride was made by Dougherty and Hammond.[80] These investigators found that the products were diphenyl sulphide and thianthrene, and the ratio in which these two compounds were formed depended to a marked degree upon the proportion of aluminum chloride employed. When the amounts of reactants were kept constant, increasing the quantity of aluminum chloride to 0.2-0.3 mole increased the yield of both sulphur compounds. From there on the yield of diphenyl sulphide increased while that of thianthrene decreased. This is illustrated by the results given in Table 105.

TABLE 105.—*Yields of Diphenyl Sulphide and Thianthrene from Benzene (200 cc.) and Sulphur (32 g.).*

Moles of Aluminum Chloride	Moles of Diphenyl Sulphide	Moles of Thianthrene
0.1	0.032	0.1
0.2	0.062	0.179
0.3	0.147	0.125
0.4	0.215	0.118
0.5	0.310	0.068
0.6	0.310	0.068
0.8	0.361	0.046
1.0	0.350	0.053

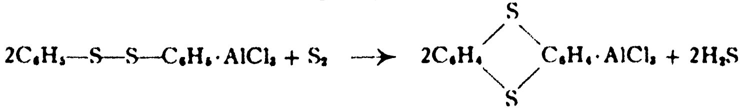
Reactions for the formation of these two compounds can be represented as follows: For diphenyl sulphide

$$S_2 \cdot AlCl_3 + C_6H_6 \cdot AlCl_3 \longrightarrow C_6H_5{-}S{-}S{-}H \cdot AlCl_3 + AlCl_3$$

$$C_6H_5{-}S{-}S{-}H \cdot AlCl_3 + C_6H_6 \cdot AlCl_3 \longrightarrow C_6H_5{-}S{-}C_6H_5 \cdot AlCl_3 + AlCl_3 + H_2S$$

and for thianthrene

$$2C_6H_5{-}S{-}C_6H_5 \cdot AlCl_3 + S_2 \longrightarrow 2C_6H_5{-}S{-}S{-}C_6H_5 \cdot AlCl_3$$



With aromatic ketones, in the absence of catalysts, the course of the reaction appears to be governed largely by the temperature. For example, benzophenone and sulphur at 155-175°C. (in an atmosphere of nitrogen) furnish biphenylacyl, and at 180-210°C. thioindigo is also obtained.[81] In a similar manner, the products from α- or β-acetonaphthone are 1,2- and 2,1-naphthothioindigo. Also coumarin may be treated with sulphur at 220-230°C. for a period of 48 hours to furnish a thiophene derivative ($C_{18}H_8O_4S$), which melts at 331-331.5°C.[82]

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[77] C. J. Ramsburg, U. S. P. 1,983,399, Dec. 4, 1934, to Koppers Co. of Del.; *Brit. Chem. Abs.* B, 1936, 319; *Chem. Abs.*, 1935, 29, 564.

[78] P. H. Bodenstein, U. S. P. 1,981,161, Nov. 20, 1934, to Meigs, Bassett and Slaughter, Inc.; *Brit. Chem. Abs.* B, 1935, 948; *Chem. Abs.*, 1935, 29, 563.

[79] French P. 787,810, 1935, to Alexander and Posnansky; *Chem. Abs.*, 1936, 30, 1068.

[80] G. Dougherty and P. D. Hammond, *J.A.C.S.*, 1935, 57, 117; *Brit. Chem. Abs.* A, 1935, 334; *Chem. Abs.*, 1935, 29, 1402; *J. Inst. Pet. Tech.*, 1935, 21, 90A. *Cf.* J. Böeseken, *Rec. trav. chim.*, 1905, 24, 209; *J.C.S.*, 1905, 88 (1), 583; *Chem. Zentr.*, 1905, 2, 227.

When sulphur is added to potassamide dissolved in liquid ammonia, a yellow precipitate is first formed which redissolves on the further addition of sulphur.[83] The reaction appears to be represented by

$$6KNH_2 + 3S \longrightarrow S(NK)_2 \cdot NH_3 + K_2S \text{ (insoluble)}$$

or if carried out rapidly

$$6KNH_2 + 12S \longrightarrow S_4(NK)_2 + 4NH_3 + K_2S_4$$

Incorporation of sulphur slowly also yields some potassium trisulphide.

In studying the action of carbon tetrachloride on sulphur,[84] chlorides of iron, aluminum or copper were employed as catalysts and the temperature maintained at 120°C. It was stated that the reaction results in the production of carbon disulphide and sulphur monochloride, and that the two latter substances also interact to give the original reactants. Equilibrium was said to be represented as:

$$6S + CCl_4 \underset{77.4\%}{\overset{22.4\%}{\rightleftarrows}} CS_2 + 2S_2Cl_2$$

Although, as previously mentioned, the presence of elemental sulphur in gasoline is objectionable, nevertheless addition of a small proportion (0.01-0.05 per cent) of this element, or of selenium or tellurium, to lubricating oils is recommended.[85] A stable emulsion of sulphur, particularly in oils intended for cutting operations, is obtained by employing sodium oleate as the emulsifying agent.[86] In other instances, sulphurized lubricants are prepared by heating the oil and sulphur to 300-500°F. under a pressure of 75-150 pounds per square inch.[87] Prior to reaction with sulphur, oxidized paraffin wax may be incorporated with the liquid.[88]

MERCAPTANS

Sulphur-containing compounds of this type, because of the presence of the -SH group, are characterized by their acidic properties.[89] Reaction with alkalies to form mercaptides is well-known and serves as a basis for extraction of mercaptans from petroleum distillates. The distribution coefficients of some low-boiling mercaptans between a cracked naphtha (boiling 83-338°F.) and dilute aqueous caustic soda (0.417 lb. per gal.) were determined by Happel and Robertson.[90]

[81] T. W. Jezierski, *Roczniki Chem.*, 1934, **14**, 216; *Chem. Abs.*, 1935, **29**, 2161; *Brit. Chem. Abs.* **A**, 1934, 773.

[82] L. Szperl and A. Chmielnicka, *Roczniki Chem.*, 1936, **16**, 101; *Brit. Chem. Abs.* **A**, 1936, 997.

[83] F. W. Bergstrom, *Z. anorg. allgem. Chem.*, 1934, **221**, 113; *Chem. Abs.*, 1935, **29**, 4689.

[84] V. A. Fromin, *J. Gen. Chem. (U.S.S.R.)*, 1936, **6**, 852; *Chem. Abs.*, 1936, **30**, 6633.

[85] French P. 788,857, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 1993. British P. 451,372, 1936; *Brit. Chem. Abs.* **B**, 1936, 970; *J. Inst. Pet. Tech.*, 1936, **22**, 511A; *Chem. Abs.*, 1937, **31**, 534. See also, S. Sakano, Japanese P. 111,324, 1935; *Chem. Abs.*, 1936, **30**, 2366. For incorporation of dithiocarbonate in lubricating oil, see B. B. Farrington and R. L. Humphreys, U. S. P. 2,020,021, Nov. 11, 1935, to Standard Oil Co. of Calif.; *Brit. Chem. Abs.* **B**, 1936, 918; *Chem. Abs.*, 1936, **30**, 608.

[86] V. R. Abrams, U. S. P. 2,007,137, July 2, 1935, to Sulflo Corp. of America; *Chem. Abs.*, 1935, **29**, 5649.

[87] R. F. Nelson, Canadian P. 348,522, 1935, to Texaco Development Corp.; *Chem. Abs.*, 1935, **29**, 3510.

[88] B. Gallsworthy, U. S. P. 1,987,397, Jan. 8, 1935, to Texas Co.; *Brit. Chem. Abs.* **B**, 1935, 1083; *Chem. Abs.*, 1935, **29**, 1621.

[89] For the measurement of acidity of various dimercaptans in ethyl alcohol see G. Schwarzenbach and A. Epprecht, *Helv. Chim. Acta*, 1936, **19**, 169; *Chem. Abs.*, 1936, **30**, 4074.

[90] J. Happel and D. W. Robertson, *Ind. Eng. Chem.*, 1935, **27**, 941; *Chem. Abs.*, 1935, **29**, 6748; *Brit. Chem. Abs.* **B**, 1935, 887; *J. Inst. Pet. Tech.*, 1935, **21**, 369A.

Their method was as follows: The cracked naphtha, before and after shaking with half its volume of the alkali solution, was fractionated into several cuts, and the mercaptan content of each cut determined. From the data so obtained, distribution coefficients (Table 106) were calculated.

TABLE 106.—*Mercaptan Distribution Coefficients between Cracked Naphtha and Aqueous Alkali.*

Cut	End Point °F.	Mercaptan	Distribution Coefficient
1	65	Methyl	213
2	125	Ethyl	80.0
3	180	Propyl	10.7
4	235	Butyl	3.0
5	280	Amyl	1.0
6	Residue	Hexyl	0

These investigators also show that 2-stage countercurrent extraction with more dilute alkali (0.05 lb. sodium hydroxide per gal.) is effective in removing mercaptans. In the first stage the naphtha was bubbled through partially spent alkali and in the second stage the washed distillate was treated with fresh alkali in a centrifugal pump. The mercaptan contents of the naphtha before and after each treating stage are detailed in Table 107.

TABLE 107.—*Countercurrent Treating of Sour Naphtha with Aqueous Alkali.*

	Mercaptan Sulphur (lb./gal.)		
Mercaptan	Raw Naphtha	1st Stage	2nd Stage
Methyl	0.0077	0.0036	0.0009
Ethyl	0.0027	0.0014	0.0005
Propyl	0.0014	0.0013	0.0007
Butyl	0.0005	0.0006	0.0004
Amyl	0.0002	0.0002	0.0002
Hexyl	0.0003	0.0003	0.0003
Total	0.0128	0.0074	0.0030

Separation of cracked petroleum distillates into fractions containing predominately one type of mercaptans is described by Lacomble.[91] For example, a cut boiling at −12° to −7°C. was found to contain only methyl mercaptan and only ethyl mercaptan was present in a fraction boiling about 15-21°C.

Regeneration of alkali solutions, employed for the extraction of mercaptans from petroleum oils, may be accomplished by washing with an immiscible liquid in which elemental sulphur is dissolved.[92] The liquid should be a solvent for the reaction product of sulphur and the mercaptide-containing solution. Another procedure involves the use of an oxidizing agent such as sodium hypochlorite, whereby mercaptans are converted into disulphides.[93] Blowing air through the hot spent alkali is suggested also.[94]

Alcoholic, instead of aqueous, solutions of alkalies may be employed as extraction agents.[95] In this instance sufficient water is added to the alcohol to render it immiscible with the petroleum distillate. After extraction, the solvent is removed by distillation and the residue treated with steam to effect hydrolysis of the mercaptides and distillation of the resulting mercaptans.[96] Another method of recovering mercaptans comprises contacting the vapors of cracked distillates with aqueous sodium plumbite whereby lead mercaptides are formed and hydrolyzing the latter with steam.[97]

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[91] A. E. Lacombe, U. S. P. 2,009,554, July 30, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 6414; *Brit. Chem. Abs.* **B**, 1936, 683.

[92] R. E. Burk and E. C. Hughes, U. S. P. 2,020,932, Nov. 12, 1935, to Standard Oil Co. of Ohio; *Chem. Abs.*, 1936, **30**, 607. See also, R. E. Burk, U. S. P. 2,009,954, July 30, 1935, to Standard Oil Co. of Ohio; *Chem. Abs.*, 1935, **29**, 6413; *J. Inst. Pet. Tech.*, 1935, **21**, 381A; *Brit. Chem. Abs.* **B**, 1936, 680. French P. 788,470, 1935; *Chem. Abs.*, 1936, **30**, 1549.

[93] W. A. Schulze, U. S. P. 1,998,849, Apr. 23, 1935, to Phillips Petroleum Co.; *Brit. Chem. Abs.* **B**, 1936, 358; *Chem. Abs.*, 1935, **29**, 4163; *J. Inst. Pet. Tech.*, 1935, **21**, 220A.

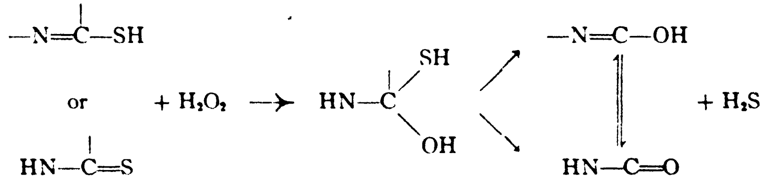
[94] L. V. Chaney and W. A. Schulze, U. S. P. 1,998,863, Apr. 23, 1935, to Phillips Petroleum Co.; *Brit. Chem. Abs.* **B**, 1936, 358; *Chem. Abs.*, 1935, **29**, 4167.

[95] W. M. Malisoff, U. S. P. 1,968,842, Aug. 7, 1934, to Atlantic Refining Co.; *Chem. Abs.*, 1934, **28**, 5975; *Brit. Chem. Abs.* **B**, 1935, 616. Canadian P. 333,899, 1933; *Chem. Abs.*, 1933, **27**, 4916.

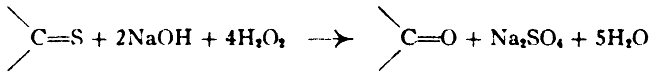
Properties of Mercaptans. As previously mentioned, the presence of the -SH group is the explanation offered for the acidic properties of mercaptans. A well-known method for their preparation is reaction of alkyl halides with alkali hydrosulphides. Application of this procedure to dihalides, however, results not only in the formation of bodies containing two -SH groups but also sulphide mercaptans.[98] For example, distillation of the product from ethylene chloride and potassium hydrosulphide gave a 45-55 per cent yield of ethylene mercaptan, $C_2H_4(SH)_2$, 16 per cent of the sulphide derivative, $HSC_2H_4SC_2H_4SH$, and 1.5 per cent of the disulphide, $HSC_2H_4SC_2H_4SC_2H_4SH$. In addition, dithiane and polymeric sulphur compounds were obtained.

Mercaptans react with many types of reagents, such as oxidizing agents (oxygen, sulphur and halogens) to form disulphides, with aldehydes and ketones to give mercaptals and mercaptoles, respectively, and with acids to yield esters.[99] Being derivatives of hydrogen sulphide probably accounts for their disagreeable odor[100] and toxicity,[101] particularly of lower-boiling mercaptans.

Oxidation. Although mild oxidation results in disulphides, more vigorous reaction furnishes sulphonic acids. Thus, *ter*-amyl mercaptan and hydrogen peroxide give the hygroscopic *ter*-pentanesulphonic acid,[102] and 2,2'-dimercaptodiethyl ether and the same reagent yield the corresponding disulphonic acid.[103] Kitamura[104] reports that when the sulphur atom is joined to a carbon atom with a double bond, oxygenated products are obtained in place of disulphides on treatment with hydrogen peroxide in an alkaline medium. He represents the reaction as



Hydrogen sulphide formed during the reaction is probably oxidized to sulphuric acid. Herrera[105] considers the reaction to be



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[96] W. M. Malisoff, U. S. P. 1,968,843, Aug. 7, 1934, to Atlantic Refining Co; *Chem. Abs.*, 1934, **28**, 5975; *Brit. Chem. Abs.* **B**, 1935, 616.

[97] W. N. Davis and M. M. Holm, U. S. P. 2,013,203, Sept. 3, 1935, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1935, **29**, 7062; *Brit. Chem. Abs.* **B**, 1936, 971.

[98] J. R. Meadow and A. E. Reid, *J.A.C.S.*, 1934, **56**, 2177; *Chem. Abs.*, 1935, **29**, 797; *Brit. Chem. Abs.* **A**, 1934, 1365.

[99] For a review of such reactions, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. For the use of ketones in refining petroleum distillates, see I. Levine, U. S. P. 1,951,324, Mar. 13, 1934, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1935, 215; *Chem. Abs.*, 1934, **28**, 3578.

[100] The odorizing of natural or water gas with a mixture of mercaptans and amino compounds is described by W. W. Odell, U. S. P. 2,032,431, Mar. 3, 1936; *Chem. Abs.*, 1936, **30**, 2730.

[101] The toxicity of methyl mercaptan was investigated by A. E. Cole, *J. Pharmacol.*, 1935, **54**, 448; *Chem. Abs.*, 1936, **30**, 1443.

[102] H. J. Backer, *Rec. trav. chim.*, 1935, **54**, 215; *Chem. Abs.*, 1935, **29**, 2914; *Brit. Chem. Abs.* **A**, 1935, 471.

[103] H. J. Backer, *Rec. trav. chim.*, 1935, **54**, 205; *Chem. Abs.*, 1935, **29**, 2915; *Brit. Chem. Abs.* **A**, 1935, 472.

[104] R. Kitamura, *J. Pharm. Soc. Japan*, 1935, **55**, 300; *Chem. Abs.*, 1935, **29**, 5810

[105] J. J. Herrera, *Anales soc. españ. fís. quím.*, 1935, **33**, 877; *Chem. Abs.*, 1936, **30**, 3349; *Brit. Chem. Abs.* **A**, 1936, 983.

Thiobenzylamide or thioacetic acid and hydrogen peroxide gave the corresponding oxygenated compounds, but the peroxide had no effect on benzyl sulphide or disulphide.

Preparation of Thioethers. At elevated temperature and in the presence of catalysts mercaptans lose hydrogen sulphide and are converted into thioethers. With activated carbon or alumina carrying cadmium or zinc sulphide, temperatures of about 300°C. are required.[106] At 150-210°C. and under 5 to 50 atmospheres, the sulphides of phosphorus or molybdenum may be employed as contact agents.[107] Before subjection to thermal treatment, substances which may act as catalyst poisons should be eliminated from mercaptans.[108] This may be accomplished by bringing the latter into contact with a solid adsorptive or polymerizing agent, e.g., activated charcoal, at 200-600°C.

Another procedure for the preparation of thioethers is that described by Lee.[109] Olefins, such as propene, butene-2, or pentene-2, are converted into the corresponding sulphuric acid esters and these in turn treated with a mercaptan. Thus, to an ester mixture comprising *ter*-amyl hydrogen sulphate, di-*ter*-amyl sulphate, and sulphuric acid (75 per cent concentration) is added ethyl mercaptan. The reactants are kept stirred until reaction is complete, overheating being carefully avoided. The oily layer, which separates, is removed, washed, neutralized, dried and distilled. The product is essentially *ter*-amyl ethyl sulphide. Klein[110] suggests utilization of the reaction between aromatic sulphonic acids and mercaptans. For example, 1,8-dilauryl thioether of anthraquinone can be made from disodium anthraquinone-1,8-disulphonate and lauryl mercaptan at a temperature of 130-160°C. and under a pressure of about 30 pounds per square inch.

The type of product obtained by combination of mercaptans and acetylene depends largely upon the catalyst employed.[111] In the presence of basic compounds vinyl thioethers are formed. Thus, when acetylene is passed into a mixture of phenyl mercaptan, *n*-butyl alcohol and potassium hydroxide (in an autoclave) until the pressure is 15 atmospheres and the reactants heated for 16 hours at 160°C., vinyl phenyl sulphide is obtained in a 91 per cent yield. If zinc acetate be added to the above-mentioned ingredients, then vinyl phenyl sulphide and *sym*-diphenyl ethylene sulphide ($C_6H_5SCH_2CH_2SC_6H_5$) are secured in 25 and 75 per cent yields, respectively. Cadmium salts may be used as catalysts in a similar manner.

Hydroxythioethers are prepared by the interaction of mercaptans with olefin oxides.[112] To illustrate, ethyl mercaptan and ethylene oxide give 2-hydroxydiethyl sulphide, and phenyl mercaptan and this oxide (in the presence of activated charcoal) unite to form phenyl-2-hydroxyethyl sulphide. At 90°C., propyl mercaptan and cyclohexene oxide yield propyl-2-hydroxycyclohexyl sulphide. Condensation of higher mercaptans, e.g., *n*-dodecyl mercaptan, and ethylene oxide (using sodium methoxide as catalyst) furnish compounds which are soluble in water and may be employed as scouring, dispersing, wetting and emulsifying agents.[113]

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[106] P. K. Frolich, U. S. P. 2,035,121, Mar. 24, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 2985. See also, C. C. Allen, U. S. P. 2,051,807, Aug. 25, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 6760.

[107] W. Seaman, U. S. P. 1,993,287, Mar. 5, 1935, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1936, 264; *Chem. Abs.*, 1935, **29**, 2547.

[108] J. R. Huffman and J. M. Whiteley, Jr., U. S. P. 1,999,612, Mar. 26, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 2976; *Brit. Chem. Abs.* **B**, 1936, 441. See also F. Schmeling, *Oel, Kohle, Erdöl, Teer*, 1936, **12** (39), 837.

[109] W. M. Lee, U. S. P. 2,020,421, Nov. 12, 1935; *Chem. Abs.*, 1936, **30**, 489.

[110] D. X. Klein, U. S. P. 2,033,339, Mar. 10, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 2986.

[111] British P. 427,903, 1935, to I. G. Farbenind. A.G.; *Brit. Chem. Abs.* **B**, 1935, 620; *J. Inst. Pet. Tech.*, 1935, **21**, 269A; *Chem. Abs.*, 1935, **29**, 6769.

[112] C. D. Nenitzescu and N. Scarlatescu, *Ber.*, 1935, **68**, 587; *Chem. Abs.*, 1935, **29**, 3979; *Brit. Chem. Abs.* **A**, 1935, 729.

[113] British P. 437,590, 1935, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1936, 88; *Chem. Abs.*, 1936, **30**, 2206. Cf. French P. 794,961, 1936; *Chem. Abs.*, 1936, **30**, 5237. Also, French

The addition of aromatic mercaptans to acetylene derivatives is described by Kohler and Potter.[114] As an example, 24.8 g. of thiocresol were added slowly to 20.4 g. of phenylacetylene, sufficient cooling being employed to prevent the reaction temperature from exceeding 100°C. The product, *p*-methyltolyl benzal sulphide ($CH_3C_6H_4SCH{=}CHC_6H_5$), exists in two isomeric forms; the one having the higher melting point (65°C.) separates on dilution of the reaction mixture with petroleum ether. After filtration and evaporation of the filtrate under reduced pressure, the other isomer (m.p. 44°C.) is obtained. The relative proportion of isomers depends upon the reaction temperature, higher temperatures favoring the formation of the low-melting isomer. The higher melting compound is slowly isomerized on distillation. Both isomers can be oxidized with hydrogen peroxide in acetic acid to give, successively, the corresponding sulphoxides and sulphones.

Photochemical Reactions of Mercaptans. Weiss and Fishgold[115] investigated the effects of radiation from a mercury arc on neutral or alkaline aqueous solutions of mercaptans. The primary reaction was considered as

$$RSH + h\nu \longrightarrow RS + H$$

Also in these solutions where a certain proportion of the anion RS^- is present, an electron transfer occurs

$$RS^-HOH + h\nu \longrightarrow RS + H + OH^-$$

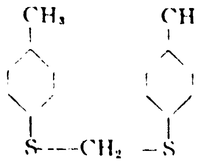
followed by

$$2H \longrightarrow H_2 \quad \text{and} \quad 2RS \longrightarrow RS{-}SR$$

The quantum efficiency with respect to the development of hydrogen was always less than unity, indicating that reverse reactions were taking place. That is, hydrogen atoms and RS radicals were recombining and also disulphides were being reduced to mercaptans. Some splitting of mercaptans into hydrocarbons and sulphur was observed.

These investigators also report that many compounds possessing a —SH group react with fluorescent dyes in the dark. On irradiating with light which is absorbed by the dye this reaction (reduction action) is accelerated. Weiss and Fishgold believe that the strong quenching effect of such sulphur compounds on fluorescent dyes is represented in principle by the reactions given above, in which the activated dye replaces the quantum.

Interaction of Mercaptans with Aldehydes and Ketones. As previously mentioned, mercaptans combine with aldehydes and ketones to form mercaptals and mercaptoles, respectively. The products obtained from aromatic mercaptans and formaldehyde, however, depend upon the relative proportions of the two reactants.[116] Thus, *p*-thiocresol (2 moles) and formaldehyde (1 mole) dissolved in acetic acid and the solution saturated with hydrogen chloride yield the oily insoluble mercaptal,



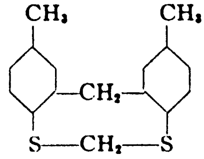
P. 749,830, 1936, to Compagnie nationale de materieres colorantes et manufactures de produits chimiques du Nord réunies, établissements Kuhlmann; *Chem. Abs.*, 1936, **30**, 5237.

[114] F. P. Kohler and H. Potter, *J.A.C.S.*, 1935, **57**, 1316; *Chem. Abs.*, 1935, **29**, 5823; *Brit. Chem. Abs.* **A**, 1935, 1115. Reaction between acetylene and mercaptans to give vinyl thioethers is discussed in Chapter 28.

[115] J. Weiss and H. Fishgold, *Nature*, 1936, **137**, 71; *Chem. Abs.*, 1936, **30**, 2494.

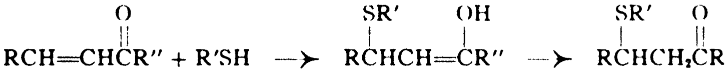
[116] W. H. Taylor, *J.A.C.S.*, 1935, **57**, 1065; *Chem. Abs.*, 1935, **29**, 5090; *Brit. Chem. Abs.* **A**, 1935, 970.

When a large excess of formaldehyde is employed, a crystalline material is obtained. It is suggested that possible condensation of the mercaptal with the aldehyde has occurred, resulting in a methylene bridge formation giving rise to a compound of the type



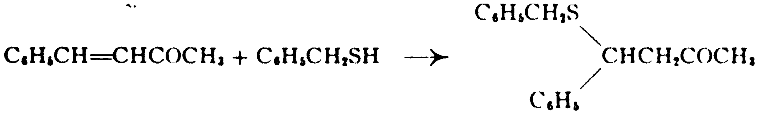
With unsubstituted aromatic mercaptans and formaldehyde (in acetic acid containing dissolved hydrogen chloride) either oily liquids (with the proper amount of aldehyde) or wax-like solids (with excess aldehyde) resulted. The waxy masses appeared to be mixtures of polymers. It was further noted that mercaptals from unsubstituted thiophenols and various other aldehydes yielded practically the same product on treatment with formaldehyde, thus indicating that the latter replaced the aldehyde residue originally present.

Mercaptans unite with α,β-unsaturated ketones to give β-ketosulphides.[117] Nicolet[118] points out that this reaction may be considered as a 1,4-addition to the conjugated series of double bonds, and can be represented as



$$RCH{=}CH\overset{\overset{O}{\|}}{C}R'' + R'SH \longrightarrow R\overset{\overset{SR'}{|}}{C}HCH{=}\overset{\overset{OH}{|}}{C}R'' \longrightarrow R\overset{\overset{SR'}{|}}{C}HCH_2\overset{\overset{O}{\|}}{C}R''$$

Furthermore, although alkaline catalysts (e.g., pyridine or sodium ethoxide) are often employed, these reactions in many instances are reversible and the initial products can be regenerated by heating the keto-sulphide with alkali. Later work[119] has shown that this condensation can take place in many cases without the aid of catalysts. For example, by gently heating a mixture of benzalacetone and benzyl mercaptan a good yield of phenyl-β-benzylmercaptopropione is obtained.



$$C_6H_5CH{=}CHCOCH_3 + C_6H_5CH_2SH \longrightarrow \begin{matrix} C_6H_5CH_2S \\ \diagdown \\ \quad CHCH_2COCH_3 \\ \diagup \\ C_6H_5 \end{matrix}$$

SWEETENING OF SOUR DISTILLATES

By sweetening of sour distillates commonly is meant the elimination of mercaptans, generally by converting them to disulphides (which, however, remain dissolved in the distillates) or by extraction with various liquid or solid media. The same purpose may be accomplished also by thermal treatment of petroleum fractions whereby mercaptans are changed to thioethers and hydrogen sulphide.

Probably the most widely used sweetening operation is the so-called "doctor sweetening" which consists essentially in agitating the sour distillate with aqueous sodium plumbite, whereby lead mercaptides soluble (for the most part) in oil are formed, and then recovering the lead as lead sulphide by the addition of sulphur. These reactions may be represented by

$$Na_2PbO_2 + 2RSH \longrightarrow 2NaOH + Pb(SR)_2$$
$$Pb(SR)_2 + S \longrightarrow PbS + RS-SR$$

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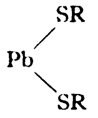
[117] For the preparation of a number of such compounds, see S. Ruhemann, *J.C.S.*, 1905, **87**, 461; *Chem. Zentr.*, 1905, 1, 1640.

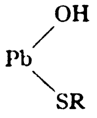
[118] B. H. Nicolet, *J.A.C.S.*, 1931, **53**, 3066; *Brit. Chem. Abs.* **A**, 1931, 1156; *Chem. Abs.*, 1931, **25**, 4850.

[119] B. H. Nicolet, *J.A.C.S.*, 1935, **57**, 1098; *Chem. Abs.*, 1935, **29**, 5090; *Brit. Chem. Abs.* **A**, 1935, 975.

Actually the reactions are not so simple as those indicated above since lead is known to form not only neutral but also basic mercaptides and these



neutral mercaptide



basic mercaptide

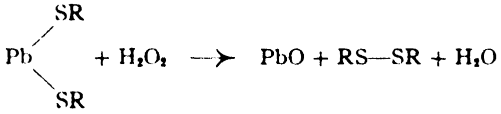
combine with sulphur to give various types of lead-sulphur compounds.[120]

In addition to lead oxide or aqueous sodium plumbite (doctor solution) other reagents have been used as sweetening agents, for example, sodium hydroxide, magnesium hydroxide (brucite), manganese dioxide, phosphorus pentoxide, hypochlorites and lead sulphide.

Perhaps the two greatest disadvantages connected with doctor and many other sweetening operations for gasolines are: (1) the resulting disulphides are soluble in the petroleum distillates thereby reducing the lead susceptibility,[121] and (2) the use of alkaline reagents often extracts phenols or other naturally occurring autoxidation inhibitors thus increasing any tendency to instability of the fuel, particularly those from cracked distillates, on storage.[122]

Use of Lead Compounds. In sweetening gasoline, Thacker[123] suggests that after agitation with doctor solution the latter be withdrawn and elemental sulphur in amount not to exceed 0.001-0.006 per cent of the gasoline be added. The liquid is then maintained in a quiescent state for 5-24 hours. Snyder[124] recommends after doctor treatment an addition of insufficient sulphur to completely precipitate lead sulphide but adequate to produce an oil of sweet odor. The oil may then be treated with clay or carbon to remove all color. Also it has been pointed out that the sulphur compounds may be removed from oils by treating the latter with doctor solution, and then passing the oil over a substance which will adsorb the lead-sulphur compounds.[125]

Instead of precipitating lead as the sulphide, decomposition of lead mercaptides by hydrogen peroxide to give lead oxide and disulphides is proposed.[126] The reaction involved in this instance may be represented as:



Another oxidizing agent which may be employed in a similar manner is potassium permanganate.[127]

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[120] For a review of the reactions involved in the sweetening operation, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[121] The effect of various sweetening operations on the antiknock properties of gasolines is discussed by C. Wirth, III, and G. B. Murphy, *Oil and Gas J.*, 1936, **34** (38) 28; *J. Inst. Pet. Tech.*, 1936, **22**, 211A; *Chem. Abs.*, 1936, **30**, 3212.

[122] For a discussion of gum formation and autoxidation inhibitors, see Chapter 40.

[123] R. B. Thacker, Jr., U. S. P. 1,994,969, Mar. 19, 1935, to Sinclair Refining Co.; *Chem. Abs.*, 1935, **29**, 3149; *Brit. Chem. Abs.* B, 1936, 261. For the determination of the amount of lead in doctor solution, see E. W. Ellis, *Refiner*, 1936, **15**, 335; *J. Inst. Pet. Tech.*, 1936, **22**, 496A.

[124] L. J. Snyder, U. S. P. 1,985,955, Jan. 1, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 1240; *Brit. Chem. Abs.* B, 1935, 1128; *J. Inst. Pet. Tech.*, 1935, **21**, 138A. F. R. Moser, Canadian P. 340,309, 1934; *Chem. Abs.*, 1934, **28**, 3887. cf. A. Belchetz, U. S. P. 2,055,423, Sept. 22, 1936; *Chem. Abs.*, 1936, **30**, 7835. French P. 796,761, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 6182.

[125] O. Codier, U. S. P. 2,042,056, May 26, 1936, to Bennett-Clark Co.; *Chem. Abs.*, 1936, **30**, 5024; *J. Inst. Pet. Tech.*, 1936, **22**, 314A.

[126] E. A. Bosing, U. S. P. 1,951,324, March 13, 1934, to Buffalo Electro Chemical Co., Inc.; *Brit. Chem. Abs.* B, 1935, 215; *Chem. Abs.*, 1934, **28**, 3574.

[127] F. B. Behrens, U. S. P. 1,927,147, Sept. 19, 1933, to Universal Oil Products Co.; *Chem. Abs.*, 1933, **27**, 5961; *Brit. Chem. Abs.* B, 1934, 789.

Removal of mercaptans may be accomplished also by using mixtures of lead oxide, sodium silicate, and borax[128] or of lead oxide and calcium hydroxide.[129] Other procedures comprise treating the sour distillate with air[130] or sodium peroxide[131] in the presence of lead sulphide suspended in aqueous alkali. An alkaline solution containing lead sulphide in suspension has also been suggested.[132] Sweetening stabilized (depropanized) naphtha with doctor solution and then contacting unstabilized naphtha with the spent solution to secure regeneration of the latter and a mercaptan-free distillate is described by Endres.[133]

By-products from Spent Doctor Solution. Valentine and MacLean[134] report that 10,500 gallons of a typical spent doctor solution contained

Lead oxide	444 lbs.
Caustic soda	5050 lbs.
Sodium thiosulphate	8510 lbs.
Phenolates	8020 lbs.
Sodium chloride	130 lbs.
Sodium carbonate	240 lbs.
Sodium sulphate and sulphite	1600 lbs.

They suggest two methods for the recovery of these compounds. In the first, lead is precipitated as the sulphide, phenols are then removed and recovered by steam distillation, and the salts are obtained by evaporation of the liquid and fractional crystallization. In the second procedure, sulphur dioxide is passed into spent doctor until the lead is eliminated. Phenols are then separated. Afterwards, sulphur is added to the solution and on evaporation sodium chloride and sulphate are salted out while the sulphites are converted into thiosulphates. The latter are obtained by cooling the hot concentrated liquor.

Thiophenols are often found admixed with the phenolic bodies from spent doctor. These sulphur-containing compounds may be removed by passage of the phenol vapors over weathered lead sludge (from plumbite solution) at temperatures approximately 55°C. higher than their boiling point.[135]

It has been proposed also to weather lead sulphide sludge for 10-12 hours, whereby lead oxide and sulphur are produced.[136]

Use of Copper Compounds. Cupric salts, in the form of ammonio-cupric derivatives, are known to react with mercaptans to furnish oil-soluble cupric mercaptides. Treatment of sour distillates with metallic copper or copper compounds is said to result in mercaptide formation.[137] This may be accelerated if the oil contains dissolved ammonia, hydrogen chloride or sulphur dioxide. In some instances, however, reduction of the cupric salts by mercaptans occurs which results in the formation of cuprous mercaptides (sometimes oil-insoluble) and organic disulphides. This latter reaction (reduction of cupric salts) is utilized by Schulze and Buell[138] who employ either solutions of or solid supric salts.

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[128] J. C. Morrell, U. S. P. 1,968,089, July 31, 1934, to Universal Oil Products Co.; *Brit Chem. Abs* **B**, 1936, 9; *Chem. Abs*., 1934, **28**, 5975.

[129] H. H. Cannon, U. S. P. 1,979,448, Nov. 6, 1934, to Cannon-Prutzman Treating Processes, Ltd.; *J. Inst. Pet. Tech.*, 1935, **21**, 65A; *Brit. Chem. Abs.* **B**, 1935, 983; *Chem. Abs.*, 1935, **29**, 329.

[130] G. L. Rowsey, U. S. P. 1,954,103, Apr. 10, 1934; *Brit. Chem Abs.* **B**, 1935, 136; *Chem. Abs.*, 1934, **28**, 3888.

[131] C. F. Teichmann, U. S. P. 2,011,954, Aug. 20, 1935, to Texas Co.; *Chem. Abs.*, 1935, **29**, 6751; *J. Inst. Pet. Tech.*, 1935, **21**, 382A; *Brit. Chem. Abs.* **B**, 1936, 778.

[132] E. S. Brown and D. B. Nutt, U. S. P. 2,049,423, Aug. 4, 1936, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 6546; *J. Inst. Pet Tech.*, 1936, **22**, 453A.

[133] A. F. Endres, U. S. P. 1,996,236, Apr. 2, 1935 to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 3509; *Brit. Chem. Abs.* **B**, 1936, 358. U. S. P. 2,022,847, Dec. 3, 1935; *Brit. Chem. Abs.* **B**, 1936, 821; *Chem. Abs.*, 1936, **30**, 851.

[134] K. S. Valentine and G. MacLean, *Refiner*, 1935, **14**, 475; *Chem. Abs.*, 1935, **29**, 8303.

[135] J. C. D. Oosterhout, U. S. P. 1,982,120, Nov. 27, 1934, to Texas Co.; *Brit. Chem. Abs.* **B**, 1935, 940; *Chem. Abs.*, 1935, **29**, 595.

[136] L. K. Adamyan, *Neft*, 1934, **5** (4), 24; *J. Inst. Pet. Tech.*, 1936, **22**, 206A; *Chem. Abs.*, 1936, **30**, 3992.

[137] G. H. von Fuchs and L. E. Borden, Canadian P. 346,402, 1934, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 2341. See also, H. P. A. Groll and G. Hearne, British P. 449,783, 1936, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1936, 917; *J. Inst. Pet. Tech.*, 1936, **22**, 404A; *Chem. Abs.*, 1936, **30**, 8598.

On contacting sour gasoline with aqueous solutions of cupric chloride, two reactions take place ultimately bringing about reduction of the cupric salt and oxidation of mercaptans to disulphides. These can be represented as:

$$\begin{aligned} 4RSH + 2CuCl_2 &\longrightarrow RS{-}SR + 2RSCu + 4HCl \\ 2RSCu + 2CuCl_2 &\longrightarrow RS{-}SR + 4CuCl \end{aligned}$$

Hydrogen chloride remains dissolved in the aqueous layer. Cuprous chloride stays suspended in the water layer, or if the latter contains a sufficiently high concentration of chloride ion the cuprous salt is dissolved. Regeneration of the solution is effected by blowing with air.

$$4CuCl + 4HCl + O_2 \longrightarrow 4CuCl_2 + H_2O$$

In the other procedure, a solid absorbent, e.g., fuller's earth, is impregnated with the cupric salt and the sour distillate filtered through it. In this instance, continuous regeneration of the agent may be effected by dissolving a predetermined amount of air in the distillate.

The use of neutral aqueous solutions of cupric salts is described by Henderson and Cowles.[139] In this instance also the spent treating agent is activated by blowing with air or oxygen.

Use of Alkaline Agents. Treatment of sour oils with substantially anhydrous alkalies, such as sodium and potassium hydroxides,[140] results in sweetening and also desulphurization. Often a small proportion of elemental sulphur is added to assist in completing the reaction, whose course is probably indicated by:

$$2RSH + S + 2NaOH \longrightarrow RS{-}SR + Na_2S + 2H_2O$$

In addition to sodium sulphide, however, some sodium polysulphide and thiosulphate are also formed. Moser[141] suggests inhibiting the corrosive action of sulphur in oils sweetened in this manner by the addition of a small quantity of an unsaturated hydroaromatic, such as tetrahydronaphthalene or cyclohexene. In other instances, the proportions of free (or elemental) and mercaptan sulphur can be adjusted prior to the alkali treat so that the resulting product is non-corrosive.[142] The use of aqueous solutions containing sodium hydroxide and sodium polysulphide (as oxidizing agent) are described by Schulze and Chanel.[143] Stagner[144] employs caustic alkali dissolved in alcohol, particularly methanol.

Another method comprises mixing petroleum distillates with a solution of sulphur in a hydrocarbon oil and conducting the mixture through a bed of brucite.[145] In this manner acidity is neutralized and mercaptans are changed to disulphides.

[138] W. A. Schulze and A. E. Buell. *Oil & Gas J.* 1935, **34** (22), 42; *J. Inst. Pet. Tech*., 1935 **21**, 452A; *Chem. Abs*., 1936, **30**, 1216; *Nat. Pet. News*, 1935, **27** (43), 24-C; *Chem. Abs*., 1936, **30**, 2737. W. A. Schulze and L. S. Gregory, *Nat. Pet. News*, 1936, **28** (41), 34. See also C. O. Hoover, U. S. P. 2,042,050 to 2,042,055, May 26, 1936, to Bennett-Clark Co.; *Chem. Abs*., 1936, **30**, 5024; *J. Inst. Pet. Tech*., 1936, **22**, 313A, 314A.

[139] L. M. Henderson and H. C. Cowles, Jr., Canadian P. 344,690, 1934, to Atlantic Refining Co.; *Chem Abs*., 1935, **29**, 2341.

[140] V. Kalichevsky, U. S. P. 2,028,335, Jan. 21, 1936, to Standard Oil Development Co.; *Chem. Abs*., 1936, **30**, 1549; *J. Inst. Pet. Tech*., 1936, **22**, 158A. cf. French P. 798,062, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs*., 1936, **30**, 7326.

[141] F. R. Moser, U. S. P. 2,031,972, Feb. 25, 1936, to Shell Development Co.; *Chem. Abs*., 1936, **30**, 2745; *J. Inst. Pet. Tech*., 1936, **22**, 213A.

[142] B. A. Stagner, British P. 425,623, 1935; *Brit. Chem. Abs.* **B**, 1935, 441; *Chem. Abs*., 1935, **29**, 5645; *J. Inst. Pet. Tech*., 1935, **21**, 219A.

[143] W. A. Schulze and L. V. Chaney, U. S. P. 2,034,837, Mar. 24, 1936, to Phillips Petroleum Co.; *Chem. Abs*., 1936, **30**, 3219; *J. Inst. Pet. Tech*., 1936, **22**, 214A.

[144] B. A. Stagner, *Ind. Eng. Chem*., 1935, **27**, 275; *Chem. Abs*., 1935, **29**, 2716; *Brit. Chem. Abs.* **B**, 1935, 535; *J. Inst. Pet. Tech*., 1935, **21**, 210A. *Oil and Gas J*., 1935, **33** (50), 62; *Chem. Abs*., 1935, **29**, 6411; *J. Inst. Pet. Tech*., 1935, **21**, 261A.

[145] E. C. Higgins and F. T. Gardner, U. S. P. 1,977,631, Oct. 23, 1934; *Brit. Chem. Abs.* **B**, 1935, 892; *J. Inst. Pet. Tech*., 1935, **21**, 26A; *Chem Abs*., 1935, **29**, 334.

Other Sweetening Agents. Hypochlorite solutions, either of the free acid or its salts, have been proposed as sweetening agents. Unless the concentration or alkalinity (in the case of salt solutions) is not carefully regulated, mercaptans in the oil may be oxidized not only to disulphides but also to sulphoxides, sulphones or sulphonic acids. Formation of sulphur chlorides may also take place. Best results are said to be obtained with reagents furnishing available chlorine in a highly dilute aqueous solution whose concentration is about 0.07 normal.[146] Catalysts, e.g., copper salts, may be added to such solutions.[147] When sulphur compounds having oxidizing properties are formed (during hypochlorite treatment) they may be reduced by the addition of mercaptans.[148] Alkyl sulphur chlorides are converted to disulphides by the action of alkali or alkaline earth sulphites, cyanides or stannites.[149]

Nisson[150] suggests a combination of doctor and hypochlorite sweetening. After agitating the sour distillate with aqueous sodium plumbite, insufficient sulphur to completely eliminate the lead as the sulphide is added. Following removal of the precipitate the oil is further treated with aqueous sodium or calcium hypochlorite. Pevere[151] recommends the use of aqueous alkaline solutions of phenol or aminophenol, and a mild oxidizing agent such as hydrogen or sodium peroxide. These peroxides may be employed also in acid solutions.[152]

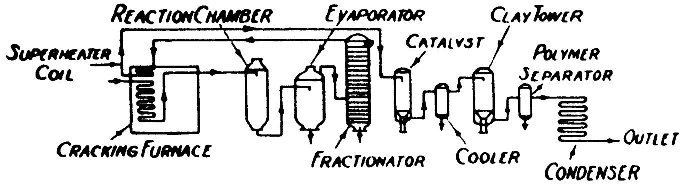

FIG. 126.—Flow Chart of Method for Removal of Mercaptans from Distillates by Conversion to Hydrogen Sulphide. (A. E. Buell and W. A. Schulze)

Passage of sour gasoline vapors over bauxite at 320-400°C. is reported to effect conversion of mercaptans to hydrogen sulphide.[153] For example, a sample of gasoline (produced by pressure cracking) with a sulphur content of 0.156 per cent (after removal of hydrogen sulphide) was conducted over bauxite at the above temperatures. The rate of flow was maintained at 6.1 barrels of gasoline per ton of bauxite. It was found that a sharp decrease in sulphur content was obtained, this reduction amounting to about 41.7 per cent. However, it was stated that the gasoline remained sweet to doctor solution until more than 500 barrels of gasoline per ton of bauxite had been desulphurized. The process is illustrated diagrammatically in Fig. 126. With cracked gasolines temperatures of 260-430°C. are used and a chromite ore as a catalyst.[154] Chromium-lead ores, such as vandite or descloizite, may be employed. The vapor-phase sweetening of gasoline with fullers' earth at 550-850°C. is described by Gray.[155] Also, it has been suggested that mercaptans in some cracked gasoline be converted into mercaptans of higher molecular weight.[156] The change was effected by passing the gasoline over active carbon, zinc sulphide and cadmium sulphide at temperatures between 250° and 350°C.

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[146] A. E. Dunstan, U. S. P. 1,999,041, Apr. 23, 1935, to Anglo-Persian Oil Co. Ltd.; *Chem. Abs.*, 1935, **29**, 4164; *J. Inst. Pet. Tech.*, 1935, **21**, 220A.

[147] G. Egloff and J. C. Morrell, U. S. P. 1,997,861, Apr. 16, 1935, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1936, 485; *Chem. Abs.*, 1935, **29**, 3818; *J. Inst. Pet. Tech.*, 1935, **21**, 220A.

[148] W. A. Schulze and L. V. Chaney, U. S. P. 2,022,942, Dec. 3, 1935, to Phillips Petroleum Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 101A; *Chem. Abs.*, 1936, **30**, 847; *Brit. Chem. Abs* **B**, 1936, 821.

[149] W. A. Schulze and L. V. Chaney, U. S. P. 2,028,998, Jan. 28, 1936, to Phillips Petroleum Co.; *Chem. Abs.*, 1936, **30**, 1987; *J. Inst. Pet. Tech.*, 1936, **22**, 158A.

[150] P. S. Nisson, U. S. P. 2,016,342, Oct. 8, 1935, to Gray Processes Corp.; *Chem. Abs.*, 1935, **29**, 8312; *J. Inst. Pet. Tech.*, 1935, **21**, 459A.

[151] E. F. Pevere, U. S. P. 2,015,038, Sept. 17, 1935, to Texas Co.; *Chem. Abs.*, 1935, **29**, 7634; *J. Inst. Pet. Tech.*, 1935, **21**, 422A; *Brit. Chem. Abs.* **B**, 1936, 969.

[152] W. M. Malisoff, U. S. P. 1,972,102, Sept. 4, 1934, to Atlantic Refining Co.; *Chem. Abs.*, 1934, **28**, 6560; *Brit. Chem. Abs.* **B**, 1935, 713.

[153] A. E. Buell and W. A. Schulze, U. S. P. 2,016,271, Oct. 8, 1935, to Phillips Petroleum Co.; *Chem. Abs.*, 1935, **29**, 8312; *J. Inst. Pet. Tech.*, 1935, **21**, 459A; *Brit. Chem. Abs.* **B**, 1936, 680.

THIOETHERS

Sulphur compounds of this type have been isolated from the acid extract obtained in treating petroleum fractions with sulphuric acid or from distillates as insoluble double compounds with mercuric chloride.[157] The boiling points and molecular heats of vaporization of some of the lower boiling thioethers were determined by Thompson and Linnett.[158] See Table 108. Application of Trouton's law[159] to these data indicates that the sulphides are normal unassociated liquids.

TABLE 108.—*Boiling Points and Heats of Vaporization of Some Thioethers.*

Thioether	Boiling Point °C.	Heat of Vaporization
Dimethyl . .	37	6910 cal.
Methyl ethyl . . .	65	7250 cal.
Diethyl	91.4	8000 cal.

Probably the most general method for the preparation of aliphatic sulphides is the reaction of alkyl halides with sodium sulphide.[160] A modification of this is the action of alkyl halides on mercaptans, thus making possible the synthesis not only of thioethers containing alkyl radicals but also those having substituted radicals. For example, from decyl mercaptan and a polyglycerol chloride there is obtained a product which, in aqueous solutions, may be employed for washing wool containing suint.[161]

Another procedure, mentioned previously, for making thioethers is the thermal decomposition of mercaptans. Elbel[162] suggests reaction between a diazotized aromatic amine and an aliphatic mercaptan possessing at least six carbon atoms. If the amine has a sulphonic acid group then the resulting sulphide exhibits saponaceous properties.

Oxidation of sulphides, first to sulphoxides and then to sulphones appears to be characteristic. Many oxidizing agents may be employed for this purpose, as for example, selenium dioxide,[163] nitric acid, potassium permanganate or bichro-

[154] A. E. Buell and W. A. Schulze, U. S. P. 2,016,272, Oct. 8, 1935, to Phillips Petroleum Co.; *Chem. Abs.*, 1935, **29**, 8312; *J. Inst. Pet. Tech.*, 1935, **21**, 459A; *Brit. Chem. Abs.* **B**, 1936, 680.

[155] T. T. Gray, U. S. P. 2,019,184, Oct. 29, 1935, to Gray Processes Corp.; *J. Inst. Pet. Tech.*, 1935, **21**, 459A; *Chem. Abs.*, 1936, **30**, 281.

[156] P. K. Frolich and P. J. Wiezevich, U. S. P. 2,045,766, June 30, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 5596.

[157] See, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. For the constitution of thioether compounds of platinum, see K. A. Jensen, *Z. anorg. allgem. Chem.*, 1935, **225**, 115; *Chem. Abs.*, 1936, **30**, 1321; *Brit. Chem. Abs.* **A**, 1936, 410.

[158] H. W. Thompson and J. W. Linnett, *Trans. Faraday Soc.*, 1935, **31**, 1743; *Chem. Abs.*, 1936, **30**, 1624; *Brit. Chem. Abs.* **A**, 1936, 149.

[159] That is, molecular heat of vaporization divided by absolute boiling temperature is a constant. Such values generally range from about 20 to 22.

[160] For the preparation of *n* propyl sulphide in this manner, see R. W. Bost and M. W. Conn, "Organic Syntheses," John Wiley & Sons, New York, 1935, **15**, 72.

[161] British P. 437,590, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 2206.

[162] E. Elbel, German P. 614,311, 1935, to Henkel & Cie, G.m.b.H.; *Chem. Abs.*, 1935, **29**, 5862; cf. E. Elbel and A. Kirstahler, U. S. P. 1,987,526, Jan. 8, 1935, to Henkel and Cie, G.m.b.H.; *Chem. Abs.*, 1935, **29**, 1436. German P. 620,889, 1935; *Chem. Abs.*, 1936, **30**, 1812.

[163] N. N. Mel'nikov, *Uspekhi Khim.*, 1936, **5**, 443; *Chem. Abs.*, 1936, **30**, 5180.

mate, and hydrogen peroxide. Böeseken and Arrias[164] used peracetic acid with aromatic sulphides. They noted that the first reaction, formation of sulphoxides, was several hundred times as rapid as the latter, that is, conversion to sulphones. Furthermore, the velocity coefficient increased with increasing concentrations of the acid. Similar observations were made with *p*-bromophenyl thioether, though the rates of reaction with this compound were much less than for the diphenyl analogue.

DISULPHIDES

Although these compounds are known to exist in crude petroleum, or its distillates, their presence in refined products can be attributed also in a large measure as a result of the sweetening operation. This is particularly true of gasoline and kerosene fractions. As pointed out before, sweetening is primarily transformation of mercaptans to disulphides by mild oxidation and a number of methods have been previously described. As an example, a sour oil is subjected to the action of air in the presence of catalysts such as oxides of copper, lead, nickel, manganese or platinum.[165] Reaction can be controlled so that the hydrocarbons are unaffected.

Alkaline liquors containing dissolved mercaptides may serve as the raw material, and oxidation carried out at temperatures of about 100°C. and under a pressure of 80 pounds per square inch.[166] Separation of disulphides thus formed from the aqueous layer can be accomplished by extraction with a petroleum distillate, e.g., gas oil.[167]

Other procedures comprise vapor-phase oxidation of mercaptans at 225°C. using activated charcoal as the contact agent,[168] and the use of chloric acid (or its salts) in an aqueous medium for liquid-phase operations.[169] In the latter instance osmium tetroxide may be employed as a catalyst. Rider and Shelton[170] prepared benzoyl persulphide by mixing benzoyl chloride with aqueous sodium hydrogen sulphide, and oxidizing the product with air. Purification of the sulphide was accomplished by dissolving it in chloroform and then precipitating by the addition of alcohol.

Elbel and Kirstahler[171] reduced disulphides to the corresponding mercaptans by boiling with aqueous sodium hydrosulphide.

Although the presence of disulphides in refined gasolines is less objectionable than that of mercaptans from the standpoint of odor, nevertheless disulphides do exert a deleterious effect on the lead susceptibility or lead response of such fuels. For instance, Schulze and Buell[172] report addition of 1 cc. of lead tetraethyl to 1 gallon of a gasoline increased its octane number by 12.5, but that incorporation of 0.41 per cent by weight of sulphur as ethyl disulphide to the leaded fuel reduced this gain to 4. They also point out that for aliphatic sulphur compounds the larger the alkyl radical and the more branched its structure the greater is the decrease in lead susceptibility. With some gasolines, sweetening followed by distillation to 10 per cent bottoms results in a product of 4 octane numbers higher than that secured by the reverse procedure.[173]

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[164] J. Böeseken and E. Arrias, *Rec. trav. chim.*, 1935, **54**, 711; *Chem. Abs.*, 1936, **30**, 2832; *Brit. Chem. Abs.* **A**, 1935, 1464. cf. H. J. Backer, *Rec. trav. chim.*, 1936, **55**, 17; *Chem. Abs.*, 1936, **30**, 6718.

[165] French P. 792,586, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 4311.

[166] H. G. M. Fischer, U. S. P. 2,001,715, May 21, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 4379; *Brit. Chem. Abs.* **B**, 1936, 683. German P. 607,986, 1932; *J. Inst. Pet. Tech.*, 1935, **21**, 220A.

[167] L. V. Chaney and W. A. Schulze, U. S. P. 1,998,863, Apr. 23, 1935, to Phillips Petroleum Co.; *J. Inst. Pet. Tech.*, 1935, **21**, 220A; *Chem. Abs.*, 1935, **29**, 4167.

[168] L. B. Turner, U. S. P. 2,028,303, Jan. 21, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 1393.

[169] E. Tschunkur and H. Köhler, German P. 601,642, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 894. French P. 772,002, 1934; *Chem. Abs.*, 1935, **29**, 1436. British P. 435,113, 1935; *Chem. Abs.*, 1936, **30**, 1068; *Brit. Chem. Abs.* **B**, 1935, 1037.

[170] T. H. Rider and R. Shelton, U. S. P. 2,028,246, Jan. 21, 1936, to W. S. Merrell Co.; *Chem. Abs.*, 1936, **30**, 1811.

[171] E. Elbel and A. Kirstahler, U. S. P. 2,031,529, Feb. 18, 1936, to Henkel & Cie, G.m.b.H.; *Chem. Abs.*, 1936, **30**, 2202.

[172] W. A. Schulze and A. E. Buell, *Nat. Pet. News*, 1935, **27** (41), 25; *J. Inst. Pet. Tech.*, 1935, **21**, 445A; *Chem. Abs.*, 1935, **29**, 8306.

POLYSULPHIDES

The presence of compounds of this type, as well as their formation during sweetening or acid refining operations, in petroleum distillates has been observed.[174] Generally these are high-boiling liquids, which in many instances may be concentrated by fractional distillation. Often they exhibit corrosive properties which render them undesirable constituents of petroleum products.

Diethyl trisulphide, $(C_2H_5)_2S_3$, may be obtained by heating diethyl sulphide and sulphur at 150°C.[175] Distillation of potassium ethyl sulphate and potassium sulphide yields a mixture of the alkyl di- and trisulphide, which may be transformed completely into the latter by treatment with sulphur. The trisulphide reacts with copper or mercury to give the corresponding metallic sulphide, and is oxidized by nitric acid to sulphuric and ethyl-sulphonic acids in the molecular ratio of 1:2.

Holmberg[176] reported that organic sulphides and disulphides (in alcohol) combine with sulphur in the presence of ammonia to form reddish-brown addition compounds. In the case of thioethers this reaction can be represented by

$$R_2S + xS + yNH_3 \longrightarrow R_2S_{x+1}\cdot yNH_3$$

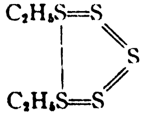
Some of these, such as the ethyl and *p*-tolyl disulphide derivatives, dissociate to furnish the tetrasulphide, sulphur and ammonia.

$$R_2S_x\cdot yNH_3 \longrightarrow R_2S_4 + S_{x-4} + yNH_3$$

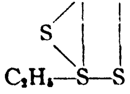
Other methods for the preparation of organic polysulphides include reaction of mercaptans with thionyl chloride,[177] thionylaniline[178] or sulphur chloride.[179]

$$\begin{aligned} 4RSH + SOCl_2 &\longrightarrow R_2S_2 + R_2S_3 + H_2O + 2HCl \\ 4RSH + C_6H_5NSO &\longrightarrow R_2S_2 + R_2S_3 + H_2O + C_6H_5NH_2 \\ 2RSH + S_2Cl_2 &\longrightarrow R_2S_4 + 2HCl \end{aligned}$$

Diethyl pentasulphide was made by heating sulphur chloride, sulphur and ethyl mercaptan (dissolved in carbon disulphide), a temperature of 150°C. giving the optimum yield.[180] Two isomers were obtained which boiled (under 26 mm. pressure) at 119°C. and 130°C., respectively. The structures suggested for these pentasulphides were



b.p. 119°C. (26 mm.)



b.p. 130°C. (26 mm.)

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[173] G. M. Woods, *Refiner*, 1935, 14, 479; *Chem. Abs.*, 1935, **29**, 8306.

[174] See, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[175] M. Müller, *J. prakt. Chem.*, 1871, (2) **4**, 40; *Chem. Zentr.*, 1871, 546; *J.C.S.*, 1871, **24**, 904.

[176] B. Holmberg, *Ber.*, 1910, **43**, 220; *Chem. Abs.*, 1910, **4**, 1047; *J.C.S.*, 1910, **98** (1), 150.

[177] B. Holmberg, *Ann.*, 1908, **359**, 84; *J.C.S.*, 1908, **94** (1), 308; *Chem. Abs.*, 1908, **2**, 1690.

[178] B. Holmberg, *Ber.*, 1910, **43**, 226; *Chem. Abs.*, 1910, **4**, 1047; *J.C.S.*, 1910, **98** (1), 165.

[179] P. Klason, *Ber.*, 1887, **20**, 3413; *J.C.S.*, 1888, **54**, 356; *Chem. Zentr.*, 1888, 246.

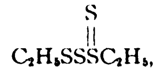
[180] G. R. Levi and A. Baroni, *Atti accad. Lincei*, 1929, (6) **9**, 772; *Chem. Abs.*, 1929, **23**, 4927; *Brit. Chem. Abs.* **A**, 1929, 1039.

The high-boiling isomer is transformed into the low-boiling at temperatures above 200°C. The former also results from the action of sulphur on diethyl di-, tri- or tetrasulphide.[181] The physical properties of the polysulphides are given in Table 109.

TABLE 109.—*Physical Properties of Diethyl Polysulphides.*

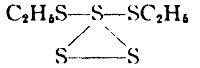
	Density	n_D^{15}	Boiling Point (at 26 mm.)
$(C_2H_5)_2S_3$	1.1140 (20°C.)	1.56899	85°C.
$(C_2H_5)_2S_4$	1.1253 (20°C.)	1.58436	109°C.
$(C_2H_5)_2S_5$ (I)	1.1687 (16°C.)	1.60269	119°C.
$(C_2H_5)_2S_5$ (II)	1.1620 (16°C.)	1.59517	130°C.

Later work by Baroni[182] on the determination of parachors[183] of various organic polysulphides (and also sulpho-selenides) indicates that di- and trisulphides possess straight chains, $C_2H_5SSSC_2H_5$, tetrasulphides a branched structure,



$$C_2H_5S\overset{\overset{\displaystyle S}{\|}}{S}SC_2H_5,$$

and pentasulphides a ring structure comprising three sulphur atoms.



A number of aliphatic mercaptans, thioethers and di- and tetrasulphides were prepared by Bezzi,[184] and some of the physical constants of these compounds determined. These values are given in Table 110.

TABLE 110.—*Physical Constants of Some Mercaptans, Thioethers and Di- and Tetrasulphides.*

Compound	Boiling Point °C.	d_4^{20}	n_D^{20}
C_2H_5SH	37°	0.8391	1.43055
C_3H_7SH	68-68.5°	0.8337	1.43908
C_4H_9SH	97-98°	0.8333	1.44402
$i\text{-}C_8H_{17}SH$	75° (18 mm.)	0.8280	1.45100
$(C_2H_5)_2S$ ...	93-94°	0.8278	1.44303
$(C_3H_7)_2S$ ..	140-143°	0.8302	1.44904
$(C_4H_9)_2S$ ..	182-184°	0.8334	1.45405
$(i\text{-}C_8H_{17})_2S$.	125.5-127° (15 mm.)	0.8332	1.46100
$(C_2H_5)_2S_2$ ..	152-154°	0.9927	1.5070
$(C_3H_7)_2S_2$ ...	191-192°	0.9525	1.4981
$(C_4H_9)_2S_2$	143-144° (83 mm.)	0.9306	1.49208
$(i\text{-}C_8H_{17})_2S_2$.	Decomp. at 190° (15 mm.)	0.86	1.4815
$(C_2H_5)_2S_4$	106-108° (24 mm.)	1.1616	1.61809
$(C_3H_7)_2S_4$	127-127.5° (11 mm.)	1.1249	1.5904
$(C_4H_9)_2S_4$ .. .	125-130° (1 mm.)	1.0775	1.5705
$(i\text{-}C_8H_{17})_2S_4$	Decomp. on heating	1.0609	1.5482

Mercaptans, thioethers and disulphides were colorless liquids with disagreeable odors. Tetrasulphides were light yellow liquids. Attempts to deodorize these sulphur compounds with copper[185] at 200-250°C., also with mercury or magnesium, were unsuccessful. Devarda alloy,[186] on the other hand, effected complete decomposition.

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[181] G. R. Levi and A. Baroni, *Atti accad. Lincei*, 1929, (6) **9**, 903; *Chem. Abs.*, 1929, **23**, 5158; *Brit. Chem. Abs.* **A**, 1929, 1039.

[182] A. Baroni, *Atti accad. Lincei*, 1931, (6) **14**, 28; *Chem. Abs.*, 1932, **26**, 1896; *Brit. Chem. Abs.* **A**, 1932, 112.

[183] The panachor is calculated according to the formula $P = (M/D - d)\ \gamma^{1/4}$ in which M is the molecular weight, D and d are the densities of the liquid and vapor phases, respectively, and γ is the surface tension in dynes per square centimeter. S. Sugden, "The Parachor and Valency," Geo. Routledge & Sons, Ltd., London, **1930**.

[184] S. Bezzi, *Gazz. chim. ital.*, 1935, **65**, 693; *Chem. Abs.*, 1936, **30**, 2171.

The atomic refraction of sulphur in these different types of compounds varied considerably, ranging from 8.761 (in tetrasulphides) to 7.95. These values, Bezzi believed, excluded the possibility of all sulphur atoms being present as chains.

Measurements of the absolute viscosities and also the viscosities of dilute solution in ether, benzene and chloroform, of the sulphur derivatives were made by Bezzi.[187] The results indicated there was a simple relation between absolute viscosity and molecular weight and this was independent of the chemical constitution. Also the viscosities of chloroform and ether solutions, of different concentrations and at different temperatures, show that the various sulphur compounds behave normally and that the lengths of the molecules (with the same alkyl radicals) are equal in mono-, di- or tetrasulphides. According to Bezzi, organic polysulphides do not contain normal chains of sulphur but constitutions similar to those proposed for inorganic polysulphides,[188] viz., a coordinated union of the alkyl groups and other sulphur atoms around one sulphur atom.

Cyclic Sulphur Compounds

The occurrence of thiophene, and its homologues, in petroleum oils or in cracked distillates has been reported by a number of investigators.[189] These sulphur compounds are isolated, for the most part, as the corresponding mercuric chloride derivatives. In chemical properties they appear to resemble benzene more than aliphatic thioethers. Thiophene, for example, yields substituted compounds with halogens rather than addition products, and nitro derivatives and sulphonic acids with nitric and sulphuric acids, respectively.

The catalytic decomposition of thiophene, in sulphur-free gasoline (boiling 80° to 100°C.), was studied by Orlov and Broun.[190] The catalysts employed were (1) a mixture of nickel, cobalt, aluminum and magnesium oxides (42:3:5:1), (2) cobalt oxide and (3) molybdenum trioxide. In each case, prior to use, the catalyst was reduced so as to give it a pyrophoric character. Afterwards the vapors of the gasoline solution mixed with hydrogen were conducted over the contact agent at a temperature of 400°C. In this manner as much as 70 per cent of the sulphur (as thiophene) was eliminated, and of the residue 50-60 per cent was composed of elemental sulphur, mercaptans, disulphides and thioethers. A nickel oxide catalyst proved best, although it eventually became poisoned by sulphur. Also, it has been suggested that carbon monoxide will remove thiophene from toluene at 300°C.[191] Molybdenum trisulphide was employed as a catalyst. It was stated that when carbon monoxide was introduced at a pressure of 1000 pounds per square inch, the sulphur content was reduced from 0.85 to 0.05 per cent. At atmospheric pressure, the proportion of sulphur was said to be reduced from 0.60 to 0.32 per cent. The use of 91-93 per cent sulphuric acid together with olefinic hydrocarbons is recommended to recover thiophene from benzene.[192]

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[185] This method was recommended by J. Finckh (*Ber.*, 1894, **27**, 1239; *J.C.S.*, 1894, **66** (1), 353, *Chem. Zentr.*, 1894, **2**, 28) for deodorization of amyl and ethyl thioethers.

[186] Devarda alloy is composed of 39 parts copper, 59 parts aluminum and 2 parts zinc. See H. Brunner and A. Rapin, *Schweiz. Wochschr.*, 1908, **46**, 455; *Chem. Abs.*, 1908, **2**, 3347; *J.C.S.*, 1908, **94** (1), 863; *Chem. Zentr.*, 1908, **2**, 676

[187] S. Bezzi, *Gazz. chim. ital.*, 1935, **65**, 693; *Chem. Abs.*, 1936, **30**, 2171.

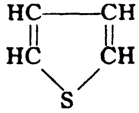
[188] See, F. K. Küster and E. Heberlein, *Z. anorg. Chem.*, 1905, **43**, 53; *Chem. Zentr.*, 1905, **1**, 497; *J.C.S.*, 1905, **88** (2), 156.

[189] See, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. A review of the preparation and properties of related substances, thiophanes and thiophthenes, is given also.

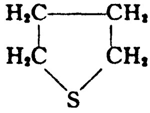
[190] N. A. Orlov and A. S. Broun, *Khim. Tverdogo Topliva*, 1932, **3**, 817; *J. Inst. Pet. Tech.*, 1935, **21**, 49A; *Chem. Abs.*, 1934, **28**, 5822; *Brit. Chem. Abs.* **B**, 1935, 12.

[191] B. W. Malishev, *J. Inst. Pet. Tech.*, 1936, **22**, 341; *Chem. Abs.*, 1936, **30**, 5773; *Brit. Chem. Abs.* **B**, 1936, 775; *J. Inst. Pet. Tech.*, 1936, **22**, 303A. See also C. M. Cawley, *J. Inst. Pet. Tech.*, **1937, 23**, 209.

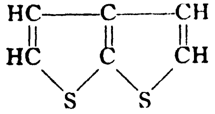
Closely allied to thiophene are thiophanes and thiophthenes. The relation between these various types is illustrated by the following formulas:



thiophene



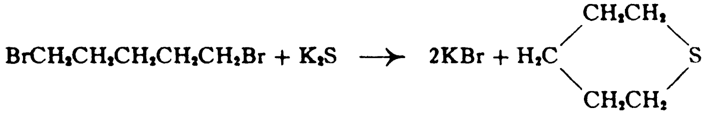
thiophane



thiophthene

Thiophanes, or hydrothiophenes, containing four or more carbon atoms have been isolated from petroleum oils or from the sulphuric acid extract (obtained in refining) as their addition products with mercuric chloride.[193] These liquid, sulphur compounds in many respects resemble thioethers in their chemical properties. They can be oxidized to sulphones, form sulphonium derivatives with alkyl halides, and addition products with metallic halides, e.g., chloroplatinates.

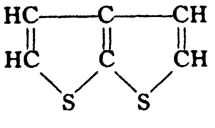
Hydrothiophenes may be prepared by the reaction of potassium sulphide with dihalogenated hydrocarbons.



In some instances, however, this method leads to the formation of polythiophanes, which are solids, of the types, $(C_8H_6S)_6$, $(C_5H_{10}S)_5$ and $(C_6H_{12}S)_4$.[194] Vigorous reduction of these polysulphides gives hydrogen sulphide and hydrocarbons, but no mercaptans. Dehydrogenation of thiophane in the presence of platinized charcoal and nickel sulphide on alumina has been reported.[195] The reaction was carried out in glass tubes 12 mm. in diameter and containing a catalyst bed 30 cm. in length. Temperatures of 315-400°C. were maintained when platinized charcoal was employed, and 350°C. with nickel sulphide. It was reported that hydrogen sulphide, olefins, paraffins, and some diolefins were obtained with both contact agents.[196]

Although the presence of thiophthenes has been suspected in coal-tar oil and shale oil, attempts to detect them have been unsuccessful. This is probably due to the fact that very little is known regarding the properties of such sulphur-containing bodies. With the object of learning more about its characteristics, Challenger and Harrison[197] prepared thiophthene by different methods and studied the materials so obtained.

One sample was made by heating a mixture of citric acid and phosphorus trisulphide.[198] The liquid product boiled at 220-221°C. and melted at 5.75-6.0°C. The structural formula assigned to it was



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[192] G. V. Kopelevich and A. I. Brodovich, Russian P. 39,096, 1934; *Chem. Abs.*, 1936, **30**, 3625.

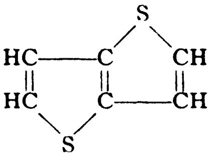
[193] See, for example, I. Teutsch, *Petroleum Z.*, 1934, **30** (20), 1; *Chem. Abs.*, 1934, **28**, 4872; *Brit. Chem. Abs.* B, 1934, 662; *Nat. Pet. News*, 1935, 27 (1), 23.

[194] R. W. Bost and M. W. Conn, *J. Elisha Mitchell Sci. Soc.*, 1934, **50**, 182; *Chem. Abs.*, 1935, **29**, 1349; *Brit. Chem. Abs.* A, 1935, 757.

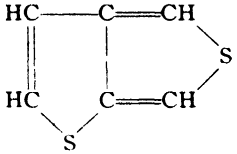
[195] Yu. K. Yur'ev and A. E. Borisov, *Ber.*, 1936, **69**, 1395; *Chem. Abs.*, 1936, **30**, 8207.

[196] B. Moldavskii and N. Prokopchuk (*J. Applied Chem. (U.S.S.R.)*, 1932, **5**, 619; *Chem. Abs.*, 1933, **27**, 274; *Brit. Chem. Abs.* A, 1933, 267) report that thiophene is transformed into butyl mer-

Another procedure employed was the reaction between sulphur and acetylene (in an atmosphere of carbon dioxide) at 440°C.[199] In this instance there were obtained carbon disulphide, thiophene, thionaphthene and two isomeric thiophthenes. Of the latter, one was a solid melting at 56°C., was called thiopheno-2',3'-3,2-thiophene, and was believed to have the formula



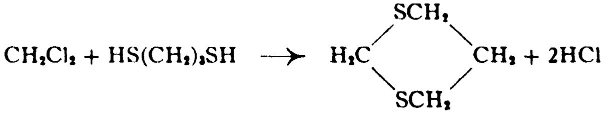
The other isomer was a liquid which boiled at 98°C. (13 mm.) and melted at 6.25-6.50°C. It probably possessed the structure indicated below, though this was not certain.



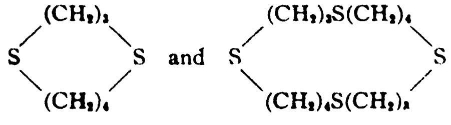
Such a compound could be designated as thiopheno-2',3'-3,4-thiophene.

All of the isomeric thiophthenes yielded characteristic addition products with picric or styphnic acid, mercurichloride derivatives, and mononitro compounds with nitric acid. With acetyl chloride and stannic chloride (as catalyst) they formed ketones which on reduction gave the corresponding ethyl thiophthene. The solid isomer (m.p. 56°C.) dissolved in alcohol and treated with sodium furnished an ethyl thiophene mercaptan, isolated as the mercury salt.

The formation of heterocyclic compounds containing two or more sulphur atoms has been observed by Meadow and Reid[200] by the action of dihalides on dimercaptans. For example, methylene chloride added to trimethylene mercaptan (in alcohol containing an equivalent quantity of sodium ethylate) yielded 1,3-dithiane.



Such reactions give rise not only to monomeric sulphur derivatives but also to polymers. Thus, from the same dimercaptan and tetramethylene bromide are secured a monomer and polymer (dimer) having the formulas,



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captan, thiophane being an intermediate product, by hydrogenation at 350°C., using molybdenum trisulphide as a catalyst.

[197] F. Challenger and J. B. Harrison, *J. Inst. Pet. Tech.*, 1935, 21, 135; *Chem. Abs.*, 1935, **29**, 4006; *Brit. Chem. Abs.* **A**, 1935, 1249; *J. Inst. Pet. Tech.*, 1935, 21, 160A.

[198] This method is described by A. Biedermann and P. Jacobson, *Ber.*, 1886, **19**, 2444; *J.C.S.*, 1886, **50**, 1032.

[199] This reaction was investigated also by J. B. Peel and P. L. Robinson, *J.C.S.*, **1928**, 2068; *Chem. Abs.*, 1928, **22**, 4460.

[200] J. R. Meadow and E. E. Reid, *J.A.C.S.*, 1934, **56**, 2177; *J. Inst. Pet. Tech.*, 1935, 21, 15A; *Brit. Chem. Abs.* **A**, 1934, 1365; *Chem. Abs.*, 1935, **29**, 797.

respectively. Depolymerization of the latter was accomplished by heating in the presence of hydrogen chloride.

UTILIZATION OF SULPHUR COMPOUNDS

Mention has been made of the possibility of converting hydrogen sulphide to sulphuric acid, and also of oxidizing aqueous alkali sulphides to thiosulphates. It has also been pointed out that elemental sulphur may be incorporated with some types of lubricants. When such incorporation is accompanied by the application of heat, the sulphur compounds resulting from the interaction of petroleum hydrocarbons and sulphur are said to be anti-oxidants.[201] The sulphur-containing bodies resulting from the hydrolysis of acid sludge (from the sulphuric acid refining of petroleum distillates) may be employed as denaturants for ethyl alcohol[202] or ethyl esters.[203]

Thioethers, and polysulphides, have been suggested as ingredients for fumigants[204] and, either alone or blended with other liquids, as solvents for rubber.[205] In the latter instance the solutions are said to be less viscous than those of the same concentration in carbon disulphide. Benzyl sulphide is reported to inhibit corrosion of aluminum by hydrochloric acid.[206] Various applications are suggested for the derivatives of thioethers. For example, dimethylethylsulphonium methylsulphate may be employed as a decolorizing agent for textiles.[207] Triethylsulphonium hydroxide may be used to loosen carbon deposits.[208] According to Kurtz,[209] dibutyl sulphone can be used for the extraction of naphthenic hydrocarbons from mineral oils.

Disulphides, such as ditolyl disulphide, mixed with thioethers or mercaptans, are said to furnish flotation agents for copper ores.[210] Taveau[211] finds that the ignition of Diesel fuels is accelerated by incorporation of 0.5 to 5 per cent of tetrasulphides.

Because of their greater chemical activity, mercaptans have found more applications probably than other types of sulphur compounds. The ease with which they are oxidized is well-known, and is possibly the basis for their use as oxidation inhibitors. About 1 per cent of a mixture of amyl mercaptan and dibutyl amine may be employed as a gum inhibitor for motor fuels derived from cracked distillates.[212] Other organic substances containing —SH groups may serve as

[201] British P. 435,548, 1935, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech.*, 1935, **21**, 459A; *Brit. Chem. Abs.* **B**, 1935, 1127; *Chem. Abs.*, 1936, **30**, 1555. See also British P. 442,161, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 5026. Also E. W. Fuller and B. W. Story, U. S. P. 1,963,489, June 19, 1934, to Vacuum Oil Co.; *Chem. Abs.*, 1934, **28**, 5224; *Brit. Chem. Abs.* **B**, 1935, 340. R. L. Humphreys and B. F. Farrington, U. S. P. 2,073,841, March 16, 1937, to Standard. Oil Co. of Calif.

[202] W. H. Hampton, U. S. P. 1,988,007, Jan. 15, 1935, to Standard Oil Co. of Calif.; *Brit. Chem. Abs.* **B**, 1936, 425; *Chem. Abs.*, 1935, **29**, 1576.

[203] W. H. Hampton, U. S. P. 1,995,539, Mar. 26, 1935, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1935, **29**, 2974; *Brit. Chem. Abs.* **B**, 1936, 920.

[204] E. C. Williams, Canadian P. 353,986, 1935, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 1472.

[205] W. Seaman and G. L. Matheson, U. S. P. 1,996,001, Mar. 26, 1935, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1936, 339; *Chem. Abs.* 1935, **29**, 3551.

[206] H. Roehrig, *Rev. Met.*, 1936, **30**, 577; *Brit. Chem. Abs.* **B**, 1936, 327.

[207] French P. 791,217, 1935, to Imperial Chemical Industries, Lt.; *Chem. Abs.*, 1936, **30**, 3254.

[208] H. E. Buc and R. Rosen, U. S. P. 2,047,191, July 14, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 6095.

[209] S. S. Kurtz, Jr., U. S. P. 2,033,942, Mar. 17, 1936, to Atlantic Refining Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 215A; *Chem. Abs.*, 1936, **30**, 3220. Canadian P. 351,484, 1935; *Chem. Abs.*, 1935, **29**, 6751.

[210] F. G. Moses, R. W. Hess and R. L. Perkins, U. S. P. 2,027,357, Jan. 7, 1936, to Barrett Co.; *Chem. Abs.*, 1936, **30**, 1347.

[211] R. deM. Taveau, U. S. P. 2,034,643, Mar. 17, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 3206.

[212] R. E. Burk, U. S. P. 2,033,877, Mar. 10, 1936, to Standard Oil Co. of Ohio; *Chem. Abs.*, 1936, **30**, 3223. For the use of amyl mercaptan as a corrosion inhibitor, see C. A. Mann, *Trans. Electrochem. Soc.*, 1936, **69**, 354; *Chem. Abs.*, 1936, **30**, 4140; *Brit. Chem. Abs.* **B**, 1936, 743.

stabilizing agents for solutions of aromatic amino-hydroxy, polyhydroxy or polyamino compounds,[213] or for the prevention of peroxidase in the darkening of apples.[214]

Incorporation of mercaptans, which may be admixed with phenols, with alkali polysulphides and an emulsifying agent (naphthenic or sulphonic acids) yields insecticidal and fungicidal compositions.[215] Another procedure involves impregnating fuller's earth, acid-treated clay or silica gel with mercaptans and disulphides.[216]

The preparation of aralkyl thiocarbonates from the corresponding mercaptans is described by Hess.[217] For example, to 24.8 parts of benzyl mercaptan and 18.2 parts of carbon disulphide are added 10.8 parts of sodium hydroxide solution (74 per cent) and 12 parts of carbon disulphide. After stirring for one-half hour the mixture is allowed to evaporate to dryness at room temperature. The residual sodium salt of benzyltrithiocarbonate, $C_6H_5CH_2SCSSNa$, is a mass of yellow crystals which can be recrystallized from alcohol. Treatment of the salt with iodine or with alkyl halides gives the disulphide or alkyl esters, respectively. These various sulphur derivatives may be used as accelerators in the vulcanization of rubber or as flotation agents in the concentration of ores.

Mercaptans may serve as the starting material for the manufacture of sulphur bodies which possess detergent, wetting and emulsifying properties. The synthesis of such compounds is an application of the reaction between alkyl halides (or their derivatives) and alkali mercaptides. As an illustration, the sodium salt of dodecylmercaptoacetic acid (from the corresponding mercaptan and chloroacetic acid) is reported to possess soapy characteristics.[218] The chloro acid may be substituted by its esters.[218a] Thus, 23 parts of sodium are dissolved in 800 parts of absolute methanol and 202 parts of dodecylmercaptan then added. On incorporation of 122.5 parts of ethyl chloroacetate separation of sodium chloride begins, and reaction is completed by boiling the mixture for two hours. After removal of the precipitated salt, saponification of the product is effected by heating for one hour with alcoholic caustic soda The hot solution is neutralized with hydrochloric acid, and on cooling the sodium salt of dodecyl-thioglycolic acid is obtained as a white crystalline mass.

Organic sulphides resulting from the combination of mercaptans and esters of chlorinated carboxylic acids are suggested as softening agents for textiles.[219] An example of such is the thio compound made from dodecylchloroacetic ester and sodium phenylmercaptan. Sulphonation of aliphatic hydroxy-sulphides, from alkyl mercaptans and halohydrins, yields materials applicable as cleaning and emulsifying agents.[220]

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[213] British P. 432,480, 1935, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1935, 894, *Chem. Abs.*, 1936, **30**, 106.

[214] A. K. Balls and W. S. Hale, *Ind. Eng. Chem.*, 1935, **27**, 335; *Brit. Chem. Abs.* B, 1935, 604; *Chem. Abs.*, 1935, **29**, 3062.

[215] A. G. V. Berry, British P. 428,542, 1935, to Trinidad Leaseholds, Ltd.; *Chem. Abs.*, 1935, **29**, 6692; *J. Inst. Pet. Tech.*, 1935, **21**, 313A; *Brit. Chem. Abs.* B, 1935, 743.

[216] T. R. Remy, U. S. P. 1,986,218, Jan. 1, 1935, to Texas Co.; *Chem. Abs.*, 1935, **29**, 1205; *Brit. Chem. Abs.* B, 1936, 387.

[217] R. W. Hess, U. S. P. 2,021,726, Nov. 19, 1935, to National Aniline & Chemical Co., Inc.; *Chem. Abs.*, 1936, **30**, 487.

[218] E. Elbel and E. L. Müller, U. S. P. 2,050,169, Aug. 4, 1936, to Henkel and Cie. G.m.b.H.; *Chem. Abs.*, 1936, **30**, 6853. French P. 748,460, 1933; *Chem. Abs.*, 1933, **27**, 5340.

[218a] E. Elbel and A. Kirstahler, U. S. P. 1,987,526, Jan. 8, 1935, to Henkel & Cie. G.m.b.H.; *Chem. Abs.*, 1935, **29**, 1436. British P. 412,305, 1933; *Brit. Chem. Abs.* B, 1934, 751; *Chem. Abs.*, 1934, **28**, 7594. *Cf.* German P. 619,299, 1935; *Chem. Abs.*, 1936, **30**, 1385.

[219] British P. 403,882, 1934, to Henkel & Cie. G.m.b.H.; *Chem. Abs.*, 1934, **28**, 3424; *Brit. Chem. Abs.* B, 1934, 355.

[220] A. W. Baldwin and H. A. Piggott, British P. 435,039, 1935, to Imperial Chemical Industries Ltd.; *J. Inst. Pet. Tech.*, 1935, **21**, 424A; *Brit. Chem. Abs.* B, 1935, 1131; *Chem. Abs.*, 1936, **30**, 1152.

According to Derby and Cunningham,[221] a flotation agent can be prepared in the following manner: Naphthalene is treated with phosphorus pentasulphide to furnish a naphthalenethiophosphoric anhydride. This in turn is reacted with phenol and the resulting product is combined with organic nitrogenous bases.

DESULPHURIZATION OF PETROLEUM DISTILLATES

Any attempt to completely survey refining operations applicable to various petroleum fractions is without the scope of this text. Indeed, limiting refining to the desulphurization of low-boiling distillates, particularly gasoline and kerosene, still embraces a wide field. However, as many developments in processes involving sulphur removal represent applications of the chemical reactions (just discussed) in which the various sulphur compounds take part, a brief summary of some of these methods is included.

Solvent extraction with concentrated sulphuric acid is well known. The disadvantages connected with the ordinary use of this agent, e.g., oxidation, polymerization of olefinic hydrocarbons, sulphation and sulphonation, have stimulated efforts towards the amelioration of such effects or the substitution of other agents. Davis and Hampton[222] suggest countercurrent treatment of distillates, the temperature being always less than —6°C. The employment of dilute sulphuric acid (35 to 80 per cent) which is subjected to electrolysis before being brought into contact with the petroleum fraction is another procedure.[223] An organic base, such as aniline or pyridine may be added to the sulphuric acid to reduce the activity of the latter.[224] Other extraction media which have been recommended are furfuraldehyde mixed with amylamine,[225] ethylenediamine,[226] and polyhydric alcohols or ethers therefrom.[227]

Solid treating agents such as metallic chlorides have been proposed. For example, aluminum chloride at 100-150°C. is reported to polymerize selectively the sulphur compounds in gasoline, after which separation of the reaction products is accomplished by filtration, decantation or settling.[228] It has been pointed out that this reagent is particularly effective with allyl, *sec*-butyl and benzyl sulphides.[229] *n*-Heptyl and ethyl sulphides are only slightly attacked. Other chlorides which may be employed are those of copper,[229a] titanium, iron, zinc or tin.[230] Another procedure comprises conducting gasoline vapors countercurrently to a molten stream of aluminum chloride mixed with zinc or cupric chloride.[231]

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[221] J. H. Derby and O. D. Cunningham, Canadian P. 348,093, 1935, to P. C. Reilly; *Chem. Abs.*, 1935, **29**, 3288.

[222] W. N Davis and W. H. Hampton, U. S. P. 1,977,717, Oct. 23, 1934, to Standard Oil Co. of Calif.; *Brit. Chem. Abs.* **B**, 1935, 983; *Chem. Abs.*, 1935, **29**, 322.

[223] E. W. Hultman, U. S. P. 1,992,308, 1,992,309 and 1,992,310, Feb. 26, 1935, to Hultman and Powell Corp.; *Chem. Abs.*, 1935, **29**, 2732; *J. Inst. Pet. Tech.*, 1935, **21**, 175A

[224] J. C. Morrell, U. S. P. 2,049,016, July 28, 1936, to Universal Oil Products Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 453A; *Chem. Abs.*, 1936, **30**, 6546.

[225] R. E. Manley and H. H. Gross, U. S. P. 1,971,753, Aug. 28, 1934, to Texas Co.; *Brit. Chem. Abs.* **B**, 1935, 713; *Chem. Abs.*, 1934, **28**, 6560.

[226] E. A. Ocon, Canadian P. 358,236, 1936; *Chem. Abs.*, 1936, **30**, 5026.

[227] W. M. Malisoff, U. S. P. 2,013,663, Sept. 10, 1935, to Atlantic Refining Co.; *J. Inst. Pet. Tech.*, 1935, **21**, 422A; *Chem. Abs.*, 1935, **29**, 7064; *Brit. Chem. Abs.* **B**, 1936, 969.

[228] W. M. Malisoff, U. S. P. 1,948,528, Feb. 27, 1934, to Atlantic Refining Co.; *Chem Abs.*, 1934, **28**, 2884. *Cf.* D. R. Stevens and W. A. Gruse, U. S. P. 1,999,345, April 30, 1935, to Gulf Refining Co.; *Brit. Chem. Abs.* **B**, 1936, 777; *Chem. Abs.*, 1935, **29**, 4165. Also R. F. Davis, U. S. P. 2,024,861, Dec. 17, 1935, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1936, 821; *Chem. Abs.*, 1936, **30**, 1221.

[229] N. D. Zelinskii and Yu. K. Yur'ev, *Neft. Khoz.*, 1934, **26** (9), 36; *Chem. Abs.*, 1935, **29**, 4927; *Brit. Chem. Abs.* **B**, 1934, 402.

[229a] R. B. Day, U. S. P. 2,051,939, Aug. 25, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 6938; *J. Inst. Pet. Tech.*, 1936, **22**, 453A. Also, U. S. P. 2,001,185, May 14, 1935; *Brit. Chem. Abs.* **B**, 1936, 730; *Chem. Abs.*, 1935, **29**, 4572.

[230] W. M. Malisoff, Canadian P. 347,667, 1935, to Atlantic Refining Co.; *Chem. Abs.*, 1935, **29**, 3148. See also G. Egloff, U. S. P. 2,009,879, July 30, 1935, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1936, 680; *Chem. Abs.*, 1935, **29**, 6414.

[231] M. C. Sumpter, U. S. P. 1,971,167, Aug. 21, 1934, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1936, 86; *Chem. Abs.*, 1934, **28**, 6295.

Desulphurization by alkalies has been accomplished, for example, by heating natural or cracked benzines, benzene or other motor fuels, under pressure with water solutions of sodium hydroxide.[232] According to Rosenstein,[233] sulphur compounds are removed by liquid ammonia and if alkali cyanides are added to the latter thiocyanates are obtained as by-products. Subjection of gasoline vapors, mixed with gaseous ammonia, to heated activated carbon[234] or to molten sodium or calcium[235] likewise has been proposed. Pines[236] effects removal of a large proportion of sulphur from cracked distillates with sodamide. For example, vapor-phase treatment of a cracked California gasoline with sodamide at 500-510°F. reduced the sulphur content from 0.56 to 0.23 per cent.

When vapors of sulphur-containing oils are brought into contact with aluminum sulphide at temperatures above 300°C. the sulphur bodies are decomposed to hydrocarbons and hydrogen sulphide.[237] Zinc sulphide, or complex compounds such as ferrous zinc sulphide, may be used in a similar manner.[238] Buell and Schulze[239] recommend bauxite at 600-750°F. as a sweetening and desulphurizing agent. The activity of this catalyst gradually decreases with use, this being more marked when cracked gasolines are treated than in the case of straight-run distillates. Reactivation may be accomplished by steaming followed by passing simultaneously air and steam at 775-800°F. through it. Other contact agents which have been proposed for the thermal decomposition of sulphur compounds are copper oxide,[240] ferric oxide,[241] silica gel[242] and adsorbent clays.[243]

Ellis[243a] points out that treatment of petroleum hydrocarbon vapors with a gaseous mixture consisting of hydrogen, methane, and carbon monoxide results in desulphurization. The proportion of hydrogen in the gas should be insufficient to produce saturated compounds. It is recommended that the operation be carried out at temperatures of 900° to 1020°F. and under a pressure of 50 atmospheres or higher. Catalysts which may be employed include the oxides of molybdenum or tungsten.

Morrell suggests vapor-phase treatment of petroleum distillates with ozone, using copper, ferric oxide or activated carbon as a catalyst.[244] Afterwards the distillate is subjected to the action of an aqueous salt solution (e.g., sodium bisulphate) containing sulphuric acid. Ozonization of gasoline in the liquid phase (at

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[232] British P. 425,938, 1935, to Gewerkschaft Mathias Stinnes; *Chem. Abs.*, 1935, **29**, 6417; *Brit. Chem. Abs.* **B**, 1935, 441. See also H. Hollings, R. H. Griffith and R. N. B. D. Bruce. British P. 452,167, 1936, to Gas, Light and Coke Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 500A. Also W. M. Malisoff, U. S. P. 2,043,254, June 9, 1936, to Atlantic Refining Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 404A; *Chem. Abs.*, 1936, **30**, 5403.

[233] L. Rosenstein, U. S. P. 1,974,724 and 1,974,725, Sept. 5, 1934, to Shell Development Co.; *Brit. Chem. Abs.* **B**, 1935, 712; *Chem. Abs.*, 1934, **28**, 7516

[234] W. L. Benedict, U. S. P. 1,971,172, Aug. 21, 1934, to Universal Oil Products Co.; *Chem. Abs.*, 1934, **28**, 6295.

[235] J. C. Morrell, U. S. P. 2,002,747, May 28, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 4931; *Brit. Chem. Abs.* **B**, 1936, 917.

[236] H. Pines, U. S. P. 1,937,914, Dec. 5, 1933, to Universal Oil Products Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 112A; *Brit. Chem. Abs.* **B**, 1934, 870; *Chem. Abs.*, 1934, **28**, 1180.

[237] W. M. Malisoff Canadian P. 344,536, 1934, to Atlantic Refining Co.; *Chem. Abs.*, 1935, **29**, 2346. U. S. P. 2,015,080, Sept. 24, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 422A; *Chem. Abs.*, 1935, **29**, 7635.

[238] W. M. Malisoff, Canadian P. 344,688, 1934, to Atlantic Refining Co.; *Chem. Abs.*, 1935, **29**, 2346.

[239] A. E. Buell and W. A. Schulze, U. S. P. 2,016,271, Oct. 8, 1935, to Phillips Petroleum Co.; *Chem. Abs.*, 1935, **29**, 8312.

[240] C. L. Smith and W. G. Annable, U. S. P. 2,032,896, Mar. 3, 1936, to Pure Oil Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 200A; *Chem. Abs.*, 1936, **30**, 2744.

[241] French P. 776,798, 1935, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1935, **29**, 3820. E. R. P. E. Retailliau and J. B. Wyman, Canadian P. 355,082, 1935, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 2362.

[242] H. Whitaker, U. S. P. 1,952,482, Mar. 27, 1934, to Petroleum Processes Corp.; *Brit. Chem. Abs.* **B**, 1935, 216; *Chem. Abs.*, 1934, **28**, 3574.

[243] F. M. Rogers, U. S. P. 2,028,995, Jan. 28, 1936, to Standard Oil Co. of Ind.; *Chem Abs.*, 1936, **30**, 1992; *J. Inst. Pet. Tech.*, 1936, **22**, 158A.

[243a] Carleton Ellis, U. S. P. 1,966,790, July 17, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1934, **28**, 5652; *Brit. Chem. Abs.* **B**, 1935, 441.

[244] J. C. Morrell, U. S. P. 1,973,500, Sept. 11, 1934, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1935, 794; *Chem. Abs.*, 1934, **28**, 6993.

—20°C.) followed by steam distillation is described by Kirsanov and Suslina.[245] The sulphur compounds are said to be converted partly into sulphuric acid and partly into non-volatile acidic and neutral bodies. Simultaneously with desulphurization there is a lowering of the iodine number and content of naphthenes, while the proportions of saturated and aromatic hydrocarbons increase. It is suggested that some gasolines contain sulphur derivatives of naphthenes and aromatics. The rate of desulphurization was not affected by water, lime, sulphuric acid or potassium dichromate.[246] Other oxidizing agents which have been proposed, particularly for cracked hydrocarbons, are aqueous solutions of an alkali pyrosulphate[247] or persulphate[248] and sulphuric acid, and oxides of nitrogen diluted with an inert gas such as carbon dioxide.[249] Hydrogen or sodium peroxide,[250] sodium persulphate mixed with alkali hydroxides or carbonates,[251] and per-acids, such as per-acetic or mono-persulphuric acid,[252] have been recommended.

The treatment of gasoline vapors with hypochlorous acid to secure a product of low sulphur and gum contents is described by Egloff.[253] Aqueous sodium hypochlorite exerts very little effect on thiophene though the free acid attacks it readily.[254] An effective solution of this acid can be prepared by adding acetic acid to a water solution of sodium hypochlorite until the p_H (glass electrode) is 3.9-4.0. This reagent appears partly to oxidize thiophene to sulphuric acid and partly to transform it to derivatives of much higher boiling points. According to Davis,[255] heterocyclic sulphur compounds are removed by subjecting the distillate to halogenation, in the presence of a catalyst, e.g., iron or aluminum, and afterwards heating with piperidine or its homologues.

Other desulphurizing agents which have been suggested are ferric sulphate,[256] metallic nitrides,[257] such as magnesium nitride, ferric nitrate,[258] and ammonium chloride vapors in the presence of zinc.[259] Maliyantz[260] reports that in many Russian crude oils the bacteria *Spirillum aestuari* produces a partial decomposition of sulphur compounds to hydrogen sulphide and sulphuric acid, and also some oxidation of the hydrocarbons. Such bacteria, however, do not act in an alkaline medium.

[245] A. V. Kirsanov and V. N. Suslina, *J. Applied Chem. (U.S.S.R.)*, 1935, **8**, 277; *Chem. Abs.*, 1936, **30**, 3977; *Brit. Chem. Abs.* **B**, 1935, 709.

[246] A. V. Kirsanov, I. M. Polyakova and Ya. N. Ivaschenko, *J. Applied Chem. (U.S.S.R.)*, 1935, **8**, 1197; *Brit. Chem. Abs.* **B**, 1936, 178; *Chem. Abs.*, 1936, **30**, 5772.

[247] J. C. Morrell, U. S. P. 1,954,487, April 10, 1934, to Universal Oil Products Co., *Chem. Abs.*, 1934, **28**, 3884; *Brit. Chem. Abs.* **B**, 1935, 136.

[248] J. C. Morrell, U. S. P. 1,954,488, April 10, 1934, to Universal Oil Products Co.; *Chem. Abs.*, 1934, **28**, 3884; *Brit. Chem. Abs.* **B**, 1935, 136.

[249] J. C. Morrell, U. S. P. 1,933,748, Nov. 7, 1933, to Universal Oil Products Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 40A; *Brit. Chem. Abs.* **B**, 1934, 748; *Chem. Abs.*, 1934, **28**, 628.

[250] J. Herzenberg, British P. 424,616, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 174A; *Brit. Chem. Abs.* **B**, 1934, 344; *Chem. Abs.*, 1935, **29**, 5260.

[251] H. V. Rees and C. F. Teichmann, U. S. P. 1,955,607, Apr. 17, 1934, to Texas Co.; *Brit. Chem. Abs.* **B**, 1935, 136; *Chem. Abs.*, 1934, **28**, 3883.

[252] J. Herzenberg, French P. 758,567, 1934; *Chem. Abs.*, 1934, **28**, 3228. British P. 424,564, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 174A; *Chem. Abs.*, 1935, **29**, 5260; *Brit. Chem. Abs.* **B**, 1935, 344.

[253] G. Egloff, U. S. P. 1,986,190, Jan. 1, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 1239.

[254] E. G. R. Ardagh and W. H. Bowman, *J.S.C.I.*, 1935, **54**, 267T; *Chem. Abs.*, 1935, **29**, 6889; *J. Inst. Pet. Tech.*, 1935, **21**, 376A; *Brit. Chem. Abs.* **B**, 1935, 885.

[255] R. F. Davis, U. S. P. 1,980,189, Nov. 13, 1934, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1935, 937; *J. Inst. Pet. Tech.*, 1935, **21**, 65A; *Chem. Abs.*, 1935, **29**, 332.

[256] T. Scott, U. S. P. 1,999,112, Apr. 23, 1935, to Refiners Ltd.; *Chem. Abs.*, 1935, **29**, 4166; *J. Inst. Pet. Tech.*, 1935, **21**, 220A. British P. 409,816, 1934; *Chem. Abs.*, 1934, **28**, 6296; *Brit. Chem. Abs.* **B**, 1934, 664. See also Z. Z. Biluchowski and R. Dobrowolski, *Przemysl. Chem.*, 1934, **18**, 309; *Brit. Chem. Abs.* **B**, 1935, 133; *Chem. Abs.*, 1935, **29**, 6411.

[257] R. E. Schaad, U. S. P. 1,954,843, Apr. 17, 1934, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1935, 135; *Chem. Abs.*, 1934, **28**, 3887.

[258] S. Comay, U. S. P. 2,045,262, June 23, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 5778; *J. Inst. Pet. Tech.*, 1936, **22**, 405A.

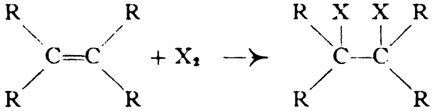
[259] R. B. Day, U. S. P. 2,029,757, Feb. 4, 1936, to Universal Oil Products Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 213A; *Chem. Abs.*, 1936, **30**, 1991.

[260] A. A. Maliyantz, *Azer. Neft. Khoz.*, **1935**, No. 6, 89; *Chem. Abs.*, 1936, **30**, 3978; *J. Inst. Pet. Tech.*, 1936, **22**, 297A.

Chapter 20

Reactions of Olefins with Halogens. Olefin Dihalides and Their Derivatives

Olefin hydrocarbons, as a class, react easily with halogens, forming addition compounds.[1] This additive capacity distinguishes them from the paraffin hydrocarbons which are capable of forming substitution derivatives only. Direct combination of the unsaturated hydrocarbons to yield olefin dihalides or dihalogen derivatives of the corresponding paraffins may be represented as:



where X is a halogen atom and R a hydrogen atom or alkyl group.[2] Interaction between monolefins and halogens is most vigorous in the case of bromine, less so with chlorine, and even less so with iodine. It also appears that the rate of halogenation of the simple monolefins increases with increasing molecular weight up to a maximum and then decreases, though constitutional influences play an important role.[3] Further, though the addition of halogens to olefins occurs rapidly, substitution also takes place to some extent with the production of polyhalogen compounds. The power of unsaturated hydrocarbons of combining directly with bromine and iodine is the basis of a number of methods of estimating these hydrocarbons, some of which are discussed in Chapter 49.

In the naming of the addition products of unsaturated hydrocarbons, some questions concerning their designation may arise. For example, dichloroethylene ($ClHC=CHCl$) may be confused with ethylene dichloride ($ClH_2C—CH_2Cl$). The former is an unsaturated compound while the latter is completely saturated. The naming of the halogenated compounds by means of the unsaturated hydrocarbon from which they are derived serves to emphasize their origin. Although ethylene dichloride and 1,2-dichloroethane are the same material the name "ethylene dichloride" has been used to designate the compound made from ethylene by addition of chlorine, and "1,2-dichloroethane" to mean that made by substitution of chlorine for hydrogen atoms in ethane. Such distinctions are purely arbitrary, however.[4] As the series of hydrocarbons is ascended and the structure of the derivatives becomes more complex, the halogen compounds can only be designated as derivatives of the hydrocarbon, preceded by a prefix indicating the nature and number of the halogen atoms. Thus, in the case of butene-1, the compound which is formed on the addition of chlorine is named 1,2-dichlorobutane.

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[1] For a discussion of the activation energies of some reactions between the halogens and the ethylene double bond, see A. Sherman and C. E. Sun, *J.A.C.S.*, 1934, **56**, 1096; *Brit. Chem. Abs.* **A**, 1934, 736; *Chem. Abs.*, 1934, **28**, 4295. J. v.Braun, *Bull. soc. chim.*, 1936, **3**, 1919.

[2] See, for example, A. Sherman, O. T. Quimby and R. O. Sutherland, *J. Chem. Phys.*, 1936, **4**, 732; *Chem. Abs.*, 1937, **31**, 94.

[3] *Cf.* Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[4] For a list of the known chlorinated derivatives of the C_1 and C_2 hydrocarbons; see Carleton Ellis, *loc. cit.*

ETHYLENE DICHLORIDE (1,2-DICHLOROETHANE)

Ethylene dichloride, $ClCH_2CH_2Cl$, has been prepared, in general, by the addition of chlorine to ethylene. The reaction may be carried out in the vapor or liquid phase, in the presence of catalysts or by employing solvents. Temperatures above 25°C. cause the rate of reaction to be increased, and under these conditions it has been found difficult to limit the reaction to direct addition, since substitution nearly always occurs.[4a]

An explanation of the mechanism by which chlorine is added to ethylene has been offered by Stewart and Weidenbaum.[5] These investigators studied the photochlorination of gaseous ethylene in the absence and presence of gases which might accept chlorine. Also they investigated the effect of solvents which could interact with chlorine, such as ethylene dichloride and pentane. Photochlorination of ethylene was carried out by conducting a mixture of ethylene and chlorine, each at a pressure of 10 cm. of sulphuric acid, into a reaction flask. The latter was illuminated by light of approximately 4360 Å, furnished by a 500-watt tungsten lamp and was evacuated to 10^{-5} mm. of mercury before the reactants were introduced. The partial pressures of each gas were measured on a sulphuric acid manometer which also served to follow the reaction rate. It was reported that the addition proceeds at a rate proportional to the chlorine concentration at constant light intensity and independent of the ethylene concentration. Accordingly, a mechanism was proposed for the reaction,

$$\begin{array}{rcl}
Cl_2 + H\nu & \longrightarrow & Cl + Cl \\
Cl + Cl_2 & \longrightarrow & Cl_3 \\
Cl_3 + C_2H_4 & \longrightarrow & C_2H_4Cl_3 \\
C_2H_4Cl_3 & \longrightarrow & C_2H_4Cl_2 + Cl \\
C_2H_4Cl_3 + W^{a} & \longrightarrow & C_2H_4Cl_2 + \frac{1}{2}Cl_2
\end{array}$$

[a] W = wall of reaction vessel.

It was pointed out that when hydrogen was added to the above reactants and interaction allowed to take place in the absence of light, there was no detectable combination between hydrogen and chlorine. In the presence of light, even with a hydrogen-ethylene ratio of 9.64:1, only 10.7 per cent of the total chlorine which reacted combined with hydrogen. This would indicate a reactivity in favor of the ethylene of about 81-fold. It was suggested that this result be interpreted in terms of the difference in the heats of activation of the two reactions. Since the heat of activation of the photochemical hydrogen-chlorine reaction is 6000 calories, that for the addition of chlorine to ethylene photochemically would be less than 1400 calories.

In studying the effect of solvents upon the combination of chlorine and ethylene, the reaction was carried out at 0°C. by immersing the reaction flask in an ice bath. At the end of a definite length of time (30 or 60 seconds), the amount of chlorine which had been chemically combined was determined by adding potassium iodide and titrating the liberated iodine with sodium thiosulphate solution. The amount of hydrogen chloride produced, which was a measure of the amount of substitution, was obtained by titrating the contents of the flask with sodium hydroxide. When pentane was employed as a solvent, it was reported that from 35.5 to 73.6 per cent of the reacting chlorine produces hydrogen chloride. Further, if at a given initial chlorine concentration the initial ethylene concentration is increased, more substitution occurs. Conversely, a relative increase in the chlorine concentration decreases substitution. The latter was said to occur probably upon the pentane, as the use of ethylene dichloride as a solvent for the same reactants produced about 10 per cent substitution as a maximum.

[4a] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[5] T. D. Stewart and B. Weidenbaum, *J.A.C.S.*, 1935, **57**, 2036; *Chem. Abs.*, 1936, **30**, 1303; *Brit. Chem. Abs.* **A**, 1936, 37.

The question was proposed as to whether the intermediate in this induced substitution of pentane is the same molecule as the intermediate in the photochemical chlorination of ethylene. A chlorine atom may be an intermediate in both the chain reaction of addition to ethylene and the chain reaction of substitution upon pentane, but, as in the case of the hydrogen-chlorine reaction, ethylene should be an efficient inhibitor for the pentane-chlorine interaction. Increasing ethylene should decrease, not increase, the substitution if chlorine atoms were responsible. Therefore, it was suggested that some derivative of ethylene is the intermediate in the substitution reaction. If chlorine atoms were competed for by both ethylene and chlorine, and if (of the two products) C_2H_4Cl promoted substitution and Cl_3 promoted addition, the data obtained could be qualitatively accounted for.

$$\begin{aligned}
Cl + Cl_2 &\longrightarrow Cl_3 \\
Cl + C_2H_4 &\longrightarrow C_2H_4Cl \\
C_2H_4 + Cl_3 &\longrightarrow C_2H_4Cl_3 \longrightarrow C_2H_4Cl_2 + Cl \\
C_2H_4Cl + Cl_2 &\longrightarrow C_2H_4Cl_3 \longrightarrow C_2H_4Cl_2 + Cl \\
C_2H_4Cl + C_5H_{12} &\longrightarrow C_2H_4 + C_5H_{11} + HCl \\
C_5H_{11} + Cl_2 &\longrightarrow C_5H_{11}Cl + Cl
\end{aligned}$$

The rates of chlorination of a number of gaseous olefins and the advantages offered by various types of apparatus have been reported.[6] It is stated that the combination of chlorine with different olefins proceeds with various velocities, the reactivity of the olefins increasing with the size of the molecule. Chlorine, if present in excess, combines primarily with the propenes and butenes rather than with ethylene, when the gases from the pyrolysis of petroleum are treated. The velocity of the chlorine as it enters the reaction zone is said to affect the yield, a high velocity favoring the production of dichlorides of all olefins present. The use of a solvent for the gaseous hydrocarbons brings about the formation of polychlorides. A lowering of the process temperature is suggested to inhibit substitution, although even at −10°C., polychlorides to the extent of 12 to 15 per cent are obtained. Combination of the reactants in the vapor phase in metallic apparatus is recommended to lower the proportion of higher chlorine derivatives. When the reaction temperature is in the range 40-50°C. and the ratio of chlorine to olefin is 1:1 by volume, from 90 to 95 per cent of the theoretical yield of dichlorides is said to be secured. Of the two types of metallic apparatus investigated, copper and iron, the former is advocated as more efficient. When an iron reaction chamber is employed, the product is stated to have a black color because of the ferrous and ferric salts which are formed. The presence of methane, hydrogen and carbon monoxide in cracking gas apparently does not interfere with the chlorination of the olefin portion, since the former gases are reported to be unaffected by the halogen.[7] Also, it was confirmed that the velocity of the chlorination of propene is so much greater than that of ethylene that a complete separation of the two dichlorides is possible. For this purpose, a method of fractional halogenation has been proposed.[8] The reaction unit consists of two iron chambers packed with iron turnings and connected by means of a tube. Cracking gas is fed into one chamber from the top and chlorine into both from the bottom. Reaction takes place in the first chamber, resulting in the chlorination of the homologues of ethylene which separate as liquids and are removed from the bottom. Ethylene, which is substantially unaffected, is then conducted into the second chamber where it is chlorinated. The temperature of the entire reaction zone is maintained between 70 and 120°C. and the yield of ethylene dichloride is reported to be 90 per cent of theoretical.

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[6] Yu. G. Mamedaliev, *Azer. Neft. Khoz.*, 1935, No. 3, 67; *Brit. Chem. Abs* B, 1936, 631; *Chem. Abs.*, 1935, **29**, 6205. For a review of the preparation and applications of ethylene chloride, see J. H. Frydlender, *Rev. prod. chim.*, 1935, **38**, 385; *Chem. Abs.*, 1935, **29**, 7935.

[7] A. F. Dobryanskii, R. A. Gutner and M. K. Shchigel'skaya, *J. Applied Chem.* (*U.S.S.R.*), 1933, **6**, 1133; *J. Inst. Pet. Tech.*, 1934, **20**, 616A; *Chem. Abs.*, 1934, **28**, 4877; *Brit. Chem. Abs.* B, 1934, 228. *Trans. State Inst. Applied Chem.* (*U.S.S.R.*), 1935, **24**, 5; *Chem. Abs.*, 1935, **29**, 7272.

[8] A. F. Dobryanskii, R. A. Gutner and M. K. Shchigel'skaya, *Trans. State Inst. Applied Chem.* (*U.S.S.R.*), 1935, **24**, 21; *Chem. Abs.*, 1935, **29**, 7271; *Brit. Chem. Abs.* B, 1936, 1032.

A similar apparatus has been suggested for a liquid phase addition of chlorine to ethylene.[9] Combination was effected at 18-24°C. by conducting ethylene and chlorine in equimolecular proportions into a solvent consisting of ethylene dichloride. Or the reactants are passed into an iron tube filled with shavings of the same metal wet with ethylene dichloride. Employment of the latter substance is said to lower the amount of kerosene required for scrubbing the reaction products and to increase the amount of dihalide secured. A mixture of trichloro- and tetrachloropropanes and butanes has also been advocated as a solvent vehicle for the above reactants.[10] In this case, the solvent vehicle is conducted into the reaction chamber near the top while the ethylene and chlorine enter near the bottom. The temperature is maintained at 5°C. and the pressure at 1 atmosphere. As soon as the olefin and halogen are dissolved the liquid mixture is removed and afterwards washed, dried and fractionated. In the last step the solvent is separated and may be employed again. This is illustrated diagrammatically in Fig. 127. The yield of ethylene dichloride is reported to be between 68 and 76 per cent of the theoretical.

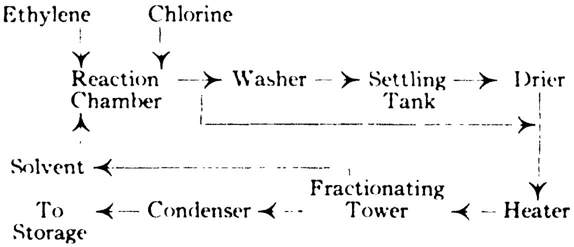

Fig. 127. Flow Sheet for Chlorination of Ethylene. (M. Berliner)

Contact agents are utilized to increase the speed of chlorination of ethylene in the vapor and liquid phases. Reynhart[11] points out that an ethylene cut, obtained from the low temperature fractionation of coke oven gas and containing 12.4 per cent of the above olefin, may be forced together with chlorine, at the rate of 1800 and 200 liters per hour, respectively through a "wetting" zone and then through a heater containing a promoter. The latter was secured by evaporating an aqueous solution of potassium ferrocyanide, aluminum chloride and ferric chloride. The temperature at the intake to the heater is 15°C., that of one-third and two-thirds of the length is 80°C. and 135°C., respectively. Upon issuing from the reaction chamber, the products were cooled to —5°C. to effect separation of the dihalides from the permanent gases. A yield of 90 per cent of the theoretical amount of ethylene dichloride was said to be gotten. In another process, catalysts are incorporated in solvents.[12] Among the former are included the chlorides of antimony, bismuth, iodine, phosphorus, sulphur, tin and manganese, and the solvent is tri- or pentachloroethane. Chlorine and gaseous olefin are led into the liquid solvent at 20°C. and 1 atmosphere pressure.

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[9] A. F. Dobryanskii and M. S. Khomutin. *Trans. State Inst. Applied Chem. (U.S.S.R.)*, 1935, **24**, 32; *Chem. Abs.*, 1935, **29**, 7271; *Brit. Chem. Abs.* **B**, 1936, 1032.

[10] M. Berliner, U. S. P. 2,022,616, Nov. 26, 1935, to Texas Co.; *Chem. Abs.*, 1936, **30**, 730; *Brit. Chem. Abs.* **B**, 1936, 1192.

[11] A. F. A. Reynhart, U. S. P. 2,043,932, June 9, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 5235. British P. 446,411, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 6757; *J. Inst. Pet. Tech.*, 1936, **22**, 368A; *Brit. Chem. Abs.* **B**, 1936, 919. French P. 801,395, 1936; *Chem. Abs.*, 1937, **31**, 416.

PROPERTIES AND USES OF ETHYLENE DICHLORIDE

Ethylene dichloride is a heavy, colorless liquid with a chloroform-like odor. It boils at 83.5°C. at 760 mm., freezes at —36°C., has d_4^{20} 1.2569, is soluble in water to the extent of 0.87 g. per 100 cc. of water at 20°C., and has a vapor pressure of 78 mm. of mercury at 20°C. In the presence of oxygen and ultraviolet light of short wave length, it is said to be converted into chloroacetic acid.[12a]

Its toxicity has been studied and compared with that of certain other organic compounds.[13] For single exposures over a period of an hour or more the poisonous effect of ethylene dichloride is reported to be of about the same order as that of benzene, carbon tetrachloride or chloroform. For periods of less than an hour it is stated to be less toxic than these compounds. A comparison with gasoline is made but since gasoline, as a commodity, may vary greatly in composition within those limits imposed by volatility and other requirements the original publication as well perhaps as the investigators themselves should be consulted for any needed data.

The odor of the dichloride vapor is distinct and noticeable in relatively safe proportions. Also, it is reported to produce marked symptoms of dizziness in concentrations that will not cause permanent injury. Since the data were obtained from a study of single exposures, no interpretation was drawn applying to the possible effects of repeated exposure. It was indicated, however, that repeated exposure would not cause a chronic type of poisoning of a nature other than the logical expectation of a possible accumulation of poisonous effects where the daily exposure is sufficient to cause the latter.

Solvent Properties. As a solvent, ethylene dichloride is said to possess many desirable characteristics, for example, high solvent power, low inflammability and availability in large quantities.[14] In the separation of mineral oils from paraffin wax, it has been suggested that the dichloride be employed alone[15] or admixed with *o*-dichlorobenzene and propene dichloride,[16] dipropyl ether,[17] methanol[18] or acetone.[19] At low temperatures (—10 to —25°C.) the dichloride or one of the compositions mentioned above is reported to dissolve the oil completely and almost none of the wax. On the other hand, it has been pointed out that ethylene dichloride is not applicable for the dewaxing of highly viscous oils.[20] The reasons advanced for this statement are the relative insolubility in ethylene dichloride of oils which have a relatively large proportion of solid paraffin present, and the selective properties of the solvent. By the second assertion is meant that some of the higher liquid hydrocarbons are relatively insoluble in ethylene dichloride and are transferred in part to the wax portion, so that the yield of dewaxed oil is lowered. The solvent properties of ethylene dichloride have been utilized in other preparations. For example, it may be employed to purify explosive substances. In one procedure the separation of di- and trinitrotoluene is brought about by dissolving a mixture of the two in 85 per cent of carbon tetrachloride and 15 per cent of ethylene dichloride. The solution is then cooled to recrystallize the trinitrotoluene, which has a higher melting point than the derivative containing two nitro groups.[21] Tetryl, or 2,4,6-trinitrophenyl methyl nitramine, may be purified by dissolving it in 1.7 times its weight of ethylene dichloride at 80°C. Upon cooling the solution to 20°C., the tetryl is said to be recrystallized.[22] Hard greases which are to be used in hot bearings are softened to some extent by the addition of a small proportion of ethylene dichloride [23] and then applied from a mechanical lubricating system. When it has been placed in the bearing the dichloride evaporates in the course of time, leaving a grease of the original consistency. An interesting use of the solvent properties of ethylene dichloride is for the extraction of white zein[24] from yellow corn. According to Mason and Palmer[25] yellow zein may be dissolved in hot 95 per cent ethanol. The addition of ethylene dichloride to this solution will effect the dissolving, in the dihalide, of any fat or pigment which is present. The decolorized zein may then be precipitated from the alcohol by incorporating acetone or ether in the latter. The last traces of color are removed from the zein by scrubbing it with ethylene dichloride. A mixture of acetic acid and the dichloride is reported to comprise a suspending vehicle for cellulose which is to be acetylated.[26] The suspension is heated and acetic anhydride incorporated, together with a small proportion of sulphuric acid which serves as a catalyst. A mixture of 80 per cent of chloroform, 16 per cent of ethylene dichloride and 4 per cent of ethanol is suggested as a solvent for water-proofing compositions.[27] The latter consists of 3.8 per cent of cellulose acetate and 11.5 per cent of hydrogenated rubber, which are incorporated in 84.7 per cent of solvent and applied to the cloth with a doctor knife. Also, it is said to be an efficient solvent for heliotropin (benzaldehyde-3,4-methylene ether) when the latter is to be converted to pyrocatechualdehyde (3,4-dihydroxybenzaldehyde).[28] The solvent properties of the dichloride have been utilized in the preparation of liquid insecticides containing rotenone.[29]

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[12] British P. 425,061, 1935, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1935, 618; *Chem. Abs.*, 1935, **29**, 5127. French P. 770,943, 1934; *Chem. Abs.*, 1935, **29**, 817.

[12a] E. Muller and K. Ehrmann, *Ber.*, 1936, **69**, 2207; *Chem. Abs.*, 1937, **31**, 93; *Brit. Chem. Abs.* **A**, 1936, 1358.

[13] R. R Sayers, W. P. Yant, C. P. Waite and F. A. Patty, *U. S. Pub. Health Repts.*, 1930, **45**, 225; *Chem. Abs.*, 1930, **24**, 2187.

[14] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. See also, E. W. Reid, U. S. P. 2,070,962, Feb. 16, 1937, to Union Carbide and Carbon Corp.

[15] L. D. Jones, U. S. P. 1,930,479, Oct. 17, 1933, to Sharples Specialty Co.; *Brit. Chem. Abs.* **B**, 1934, 791; *Chem. Abs.*, 1934, **28**, 314. British P. 447,415, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 359A; *Chem. Abs.*, 1936, **30**, 7326.

[16] B. Y. McCarty and W. E. Skelton, U. S. P. 1,995,153, March 19, 1935, to Texas Co.; *Chem. Abs.*, 1935, **29**, 3149.

[17] B. Y. McCarty and W. E. Skelton, U. S. P. 1,998,397, April 16, 1935, to Texas Co.; *Brit. Chem. Abs.* **B**, 1936, 438; *Chem. Abs.*, 1935, **29**, 3822.

[18] E. B. Hjerpe and W. A. Gruse, U. S. P. 2,042,995, June 2, 1936, to Gulf Research & Development Corp.; *Chem. Abs.*, 1936, **30**, 5022; *J. Inst. Pet. Tech.*, 1936, **22**, 406A.

[19] French P. 762,949, 1934, to Aktiebolaget Separator-Nobel; *Chem. Abs.*, 1934, **28**, 5224.

[20] D. Gol'dberg, I. Abezgauz and L. Margolis, *Azer. Neft. Khoz.*, **1935**, No. 3, 74; *Brit. Chem. Abs.* **B**, 1936, 728; *Chem. Abs.*, 1935, **29**, 6411. See also, A. Voronov and L. Kutzenok, *Novosti Nefteperarabotki*, 1936, **3** (6), 1; *Chem. Abs.*, 1936, **30**, 6930.

The conversion of ethylene dichloride to ethylene glycol, by hydrolysis with aqueous sodium carbonate, or to glycol diacetate, by heating with an anhydrous salt of acetic acid, is discussed in Chapter 22. When heated with caustic alkalies ethylene dichloride loses first one molecule of hydrogen chloride to yield vinyl chloride.

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[21] W. H. Rinkenbach, U. S. P. 1,936,607, Nov. 28, 1933; *Chem. Abs.*, 1934, **28**, 1194; *Brit. Chem. Abs.* **B**, 1934, 825.

[22] W. H. Rinkenbach and E. D. Regad, U. S. P. 1,940,811, Dec. 26, 1933; *Brit. Chem. Abs* **B**, 1934, 862; *Chem. Abs.*, 1934, **28**, 1366.

[23] W. D. Hodson, U. S. P. 2,031,368, Feb. 18, 1936; *Chem. Abs.*, 1936, **30**, 2366.

[24] Zein is a protein found in corn.

[25] I. D. Mason and L. S. Palmer, *J. Biol. Chem.*, 1934, **107**, 131; *Brit. Chem. Abs.* **A**, 1935, 268; *Chem. Abs.*, 1935, **29**, 1136.

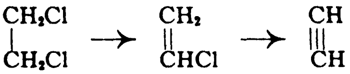
[26] C. J. Malm, Canadian P. 349,934, 1935, to Eastman Kodak Co.; *Chem. Abs.*, 1935, **29**, 4939. *Cf.* C. J. Staud and L. M. Minsk, U. S. P. 2,008,995, July 23, 1935; *Brit. Chem. Abs.* **B**, 1936, 690; *Chem. Abs.*, 1935, **29**, 6056.

[27] A. M. Alvarado, R. B. Flint and L. P. Hubbuch, U. S. P. 2,061,127, Nov. 17, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, **31**, 889.

[28] M. S. Carpenter and E. C. Kunz, U. S. P. 2,027,148, Jan. 7, 1936, to Givaudan-Delawanna. Inc.; *Chem. Abs.*, 1936, **30**, 1395.

[29] N. A. Sankowsky, U. S. P. 2,058,832, Oct. 27, 1936, to Stanco Inc.; *Chem. Abs.*, 1937, **31**, 206.

The properties and uses of this latter compound are mentioned in Chapter 28. Further treatment with caustic alkalies eventually yields acetylene, thus:

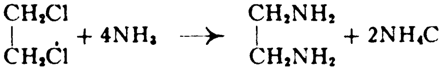


$$\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix} \rightarrow \begin{matrix} CH_2 \\ \| \\ CHCl \end{matrix} \rightarrow \begin{matrix} CH \\ ||| \\ CH \end{matrix}$$

A similar series of changes occurs when ethylene dichloride is subjected to pyrolysis at 600°C. in an atmosphere of nitrogen. Vinyl chloride and hydrogen chloride are produced (this reaction is probably reversible at lower temperatures), while at still higher temperatures acetylene is produced.[30]

Reaction of Ethylene Dichloride with Ammonia

Ethylenediamine may be produced from ethylene dichloride by interaction with ammonia, according to the equation



$$\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix} + 4NH_3 \rightarrow \begin{matrix} CH_2NH_2 \\ | \\ CH_2NH_2 \end{matrix} + 2NH_4Cl$$

Bersworth[31] suggests that liquid ammonia be heated in an autoclave to 150°C. to vaporize it and to generate a high pressure. Ethylene dichloride is then forced into the hot, compressed ammonia vapor, forming ethylenediamine hydrogen chloride (See Fig. 128). To recover the free diamine, the products are treated with caustic soda at 100°C. and conducted to an expansion chamber where the temperature is maintained at 130°C., which is above the boiling point of ethylenediamine (117°C.). The diamine vapors and unreacted ammonia are then led to a dehydrating column, where the diamine is dried and condensed. The unreacted ammonia may be recycled. In another procedure 500 g. of the dichloride, 1800 cc. of concentrated ammonium hydroxide, and 400 g. of cuprous chloride are placed in an autoclave and subjected to a temperature of 95°C. and a pressure of 150-300 lbs. per sq. in. for a period of 2 hours.[32] The copper salt is present in the reaction chamber to form a complex salt with the ethylenediamine produced. At the end of the heating period, sodium hydroxide is incorporated in the products, and the mixture is distilled. The portion boiling at 117°C. at 760 mm. is retained. It is reported that the yield of ethylenediamine is from 60 to 82 per cent of the theoretical. Other compounds which have been employed to form addition products with ethylenediamine include zinc chloride and zinc oxide.[33] To separate the diamine from its salts, it has been recommended that the latter be dissolved in liquid ammonia and then admixed with carbon dioxide.[34] In this manner the carbamate of ethylenediamine is said to be precipitated, and may be decomposed by heating with water. Mnookin[35] suggests that ethylene dichloride be treated with water and ammonia and a small proportion of ethanol to furnish ethylenediamine. The water is stated to act as a hydrolyzing agent, forming an intermediate with the dihalide with which the ammonia interacts. For example, 200 cc. of ethylene chloride, 340 cc. of concentrated ammonium hydroxide and 1600 cc. of water are heated at 140-150°C. and 150 lbs. per sq. in. for 0.5 hour to yield 40 per cent of the theoretical amount of aqueous ethylenediamine. To secure the anhydrous diamine, Bailar[36] recommended that zinc oxalate be mixed with an equivalent weight of the hydrate and the resulting compound dissolved in boiling water. On cooling the solution to 20°C. a complex crystalline salt with the formula $[ZnC_2H_4(NH_2)_2]C_2O_4$ separates. The latter is dried and heated to 200°C. under reduced pressure. At this temperature anhydrous ethylenediamine is liberated and condenses to a colorless liquid which boils between 116 and 117°C. and has d_4^{17} 0.907.

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[30] *Cf.* Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. For vinyl resins, see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[31] F. C. Bersworth, U. S. P. 2,028,041, Jan. 14, 1936, to F. Kattek; *Chem. Abs.*, 1936, 30, 1395.

[32] W. M. Lauter, U. S. P. 2,020,690, Nov. 12, 1935, to Wingfoot Corp.; *Chem. Abs.*, 1936, 30, 486; *Brit. Chem. Abs.* B, 1936, 1142.

[33] French P. 739,317, 1932; *Chem. Abs.*, 1933, 27, 2159. German P. 624,379, 1936; *Chem. Abs.*, 1936, 30, 2580. Both to Goodyear Tire & Rubber Co.

[34] P. Herold and K. Sennewald, German P. 635,397, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, 31, 117.

[35] N. M. Mnookin, U. S. P. 2,049,467, Aug. 4, 1936; *Chem Abs.*, 1936, 30, 6389.

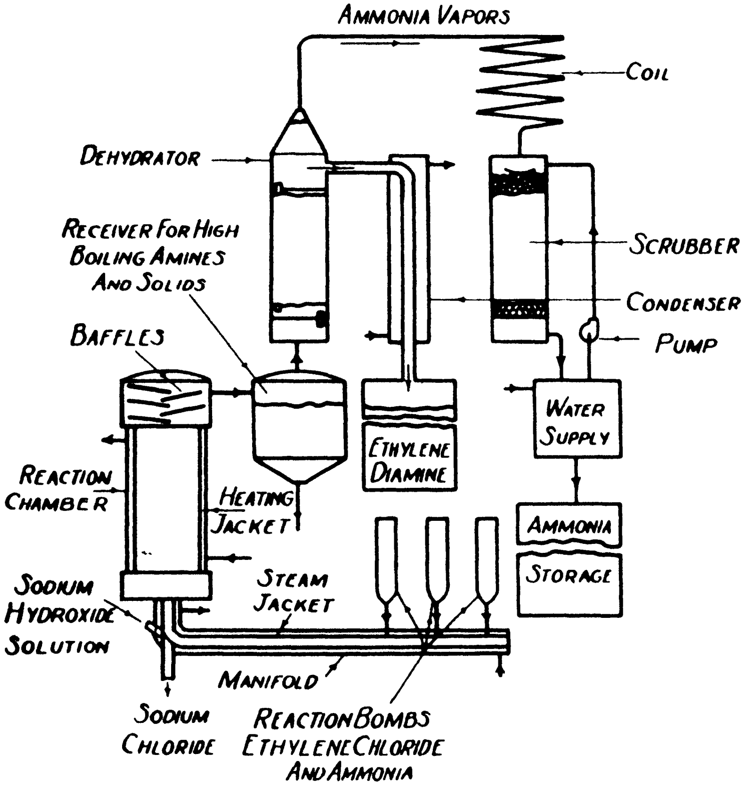

FIG. 128.—Method for Production of Ethylene Diamine from Ethylene Dichloride. (F. C. Bersworth)

Ethylenediamine has been advocated as a softening medium for the hydrolysis of cellulose acetate yarn.[37] The latter are hydrolyzed non-uniformly along their length and stretched in the presence of the diamine. In this manner hydrolysis of the parts which were not affected in the first step is said to be accomplished. Also it has been pointed out that the addition of 0.5 per cent of ethylenediamine to motor fuel will increase the antiknock properties of the latter.[38]

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[36] J. C. Bailar, Jr., *J.A.C.S.*, 1934, 56, 955; *Chem. Abs.*, 1934, 28, 3054; *Brit. Chem. Abs.* A, 1935, 637.

[37] R. W. Moncrieff and C. W. North, British P. 438,119, 1936, to British Celanese Ltd.; *Brit. Chem. Abs.* B, 1936, 96; *Chem. Abs.*, 1936, 30, 2772.

[38] E. F. Pevere, U. S. P. 2,021,088, Nov. 12, 1935, to Texas Co.; *Chem. Abs.*, 1936, 30, 606.

REACTION OF ETHYLENE DICHLORIDE WITH SULPHIDES

The reaction between ethylene dichloride and alkaline earth sulphides leads to the formation of plastic materials. For example, the dichloride may be reacted with calcium or sodium sulphide in water in the presence of magnesium hydroxide to form a latex-like dispersion of a plastic which coagulates upon acidification of the mixture. The sulphide plastics thus formed are reported to be applicable as dielectrics.[39] Ethylene dichloride will interact with polysulphides, such as sodium polysulphide, in the presence of egg-albumin and magnesium hydroxide.[40] The latter substances are employed as protective colloids for the formation of the ethylene polysulphide. In one case, 250 g. of sodium polysulphide are incorporated with 1 g. of egg-albumin, 15 g. of magnesium chloride and 6 g. of sodium hydroxide in 125 cc. of water. The mixture is then heated to 100-110°F. (38-43°C.) under a reflux condenser and ethylene dichloride added slowly. At the end of 1.5 hours the temperature is raised to 190-195°F. (88-90°C.) for a few minutes. The water-soluble products are removed by extraction with water and the ethylene polysulphide coagulated by further addition of alkali. The olefin polysulphide obtained is said to be useful in molding operations. The addition of a small proportion (0.01-1 per cent) of dibutylamine, triethanolamine and monoethanolamine to ethylene dichloride and sodium polysulphide in carbon disulphide solution has been advocated.[41] The product obtained is stated to have many properties which resemble those of natural rubber. Certain of the reactions and properties of the ethylene polysulphides have been pointed out by Patrick.[42] When the polysulphide is heated with caustic soda at 80-90°C. ethylene disulphide is said to be formed. However, the polysulphide is stated to be unaffected by boiling acetone or by sublimation under a high vacuum. Ethylene disulphide is reported to be a thermoplastic powder[43] with no definite melting point and to be unaffected by organic solvents, including carbon disulphide.

OTHER REACTIONS AND USES OF ETHYLENE DICHLORIDE

Ethylene dichloride combines with salts of aliphatic acids to form esters from which ethylene glycol may be obtained. Coleman and Moore[44] report that the diacetic ester of ethylene glycol is furnished by the interaction of ethylene dichloride and sodium acetate in the presence of a catalyst consisting of pyridine. When sodium stearate is employed in place of sodium acetate, the product is ethylene glycol distearate.[45] This latter compound, when added to a dewaxed mineral oil in the proportion of 0.1 to 1 g. of ester per 100 cc. of oil, is said to lower the pour point of the oil about 10°F.

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[39] J. C. Patrick, U. S. P. 1,950,744, March 19, 1934; *Chem. Abs.*, 1934, **28**, 3541. *Cf.* Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**.

[40] J. C. Patrick, U. S. P. 2,012,347, Aug. 27, 1935; *Chem. Abs.*, 1935, **29**, 6668. *Cf.* U. S. P. 1,990,202, Feb. 5, 1935; *Chem. Abs.*, 1935, **29**, 1903.

[41] British P. 422,826, 1935, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1935, 280; *J. Inst. Pet. Tech.*, 1935, **21**, 140A; *Chem. Abs.*, 1935, **29**, 4379. *Cf.* P. I. Pavlovich and S. M. Tartakovskii, Russian P. 39,101, 1934; *Chem. Abs.*, 1936, **30**, 5441. For a discussion of the possibilities of preparing synthetic rubber from methane, through ethylene and ethylene dichloride, see H. Pichler, *Ges. Abhandl. Kenntnis Kohle*, 1934, 11, 329; *Chem. Abs.*, 1935, **29**, 6798; *Chem. Zentr.*, 1934, **2**, 853.

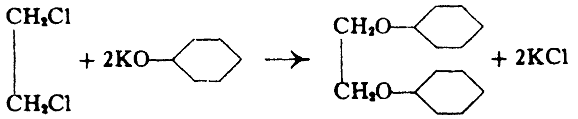
[42] J. C. Patrick, *Trans. Faraday Soc.*, 1936, **32**, 347; *Chem. Abs.*, 1936, **30**, 2462; *Brit. Chem. Abs.* **A**, 1936, 312.

[43] A thermoplastic substance is one which is adequately rigid at normal temperatures and under ordinary conditions of stress but is capable of deformation under heat and pressure. For a discussion of sulphur-olefin resins, see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**, Chapter 58.

[44] G. H. Coleman and G. V. Moore, U. S. P. 2,021,852, Nov. 19, 1935, to Dow Chemical Co.; *Chem. Abs.*, 1936, **30**, 485; *Brit. Chem. Abs.* **B**, 1936, 1192.

[45] E. F. Pevere, Canadian P. 356,637, 1936, to Texaco Development Corp.; *Chem. Abs.*, 1936, **30**, 3224.

Potassium phenolate will interact with ethylene chloride to form diphenyl ethers. In 60 cc. of water are dissolved 0.2 mole of phenol, 0.2 mole of potassium hydroxide and 25 g. of ethylene chloride. The mixture is heated under a reflux condenser for 48 hours, cooled, filtered, and the potassium chloride washed out with water. The ether so obtained is said to constitute 75-80 per cent of the theoretical amount.[46]



Also, dinaphthyl ethers may be prepared by combining the metallic salt of a naphthol with ethylene halide. For example, ethylene glycol di-β-naphthyl ether is reported to be secured by heating together (in water) sodium β-naphtholate and ethylene chloride.[47] In this instance 60 g. of caustic soda, 576 g. of β-naphthol and 198 g. of ethylene dichloride were incorporated in 600 cc. of water at 20°C. The mixture was then heated in an autoclave at 120°C. for 8 hours. At the end of this period the products were made alkaline with sodium hydroxide, and the precipitated ethylene glycol di-β-naphthyl ether, which is insoluble in water, filtered from the remaining substances. A yield of 350 g. of the dinaphthyl ether was said to be obtained.

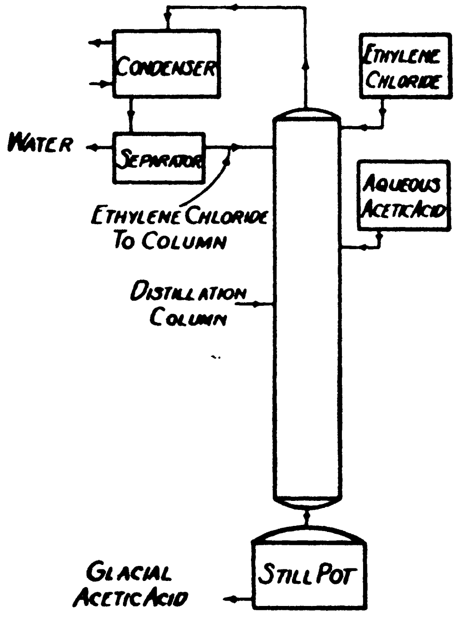


Fig. 129.
Use of Ethylene in Dehydration of Aqueous Acetic Acid. (D. F. Othmer)

The ability of ethylene dichloride to form azeotropic mixtures with water is utilized in dehydrating aqueous acids. Othmer[48] suggests the dichloride to remove the water from aqueous acetic acid. The apparatus consists of a unitary column with fractionating plates. The chloride is admitted at the top of the column and the aqueous acetic acid near the middle (see Fig. 129). In this manner an azeotropic mixture of water and the dichloride is said to be distilled, leaving anhydrous acetic acid in the residue. Aqueous solutions of propionic acid may also be distilled with ethylene chloride to bring about dehydration of the former.[49]

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[46] A. C. Cope, *J.A.C.S.*, 1935, 57, 572; *Brit. Chem. Abs.* A, 1935, 614; *Chem. Abs.*, 1935, 29, 2947.

[47] M. A. Dahlen, C. K. Black and W. L. Foohey, U. S. P. 1,979,144, Oct. 29, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 177.

In the interaction between butyl alcohol and phthalic anhydride to produce butyl phthalate, ethylene dichloride may be incorporated in the reaction zone.[50] The purpose of this addition is to form an azeotropic mixture of ethylene dichloride and the water formed by the reaction. This mixture may be distilled off during the course of the interaction. In one instance, 300 g. of butyl alcohol, 200 g. of phthalic anhydride and 125 g. of ethylene dichloride were placed in a still together with 0.6 g. of sulphuric acid, which acts as a promoter for the esterification. The reactants were heated (under reflux) at 120°C. for 30 minutes, during which time a binary mixture of water and ethylene dichloride was said to leave the top of the columns at 71-72°C. Butyl phthalate was reported to be secured in 96 per cent yield.

A motor fuel containing triethylmethane and trimethylmethane is said to be obtained by conducting a gaseous mixture of acetyl chloride, ethylene dichloride and hydrogen over a contact agent. The latter consists of iron and nickel, and the reaction temperature is in the range 250-300°C.[51]

Also, it has been reported that chlorine and ethylene dichloride, in the vapor phase at 20°C., give hexachloroethane.[52] When the two reactants unite in the liquid phase in the presence of hydrogen chloride, the compound which is formed is trichloroethane.

ETHYLENE DIBROMIDE

The thermal combination of ethylene and bromine has been studied to determine the nature of the mechanism. It was found that the gaseous reaction at 20°C. is a surface phenomenon[53] which appeared to take place by the simple addition of bromine to the double bond.[54] The order[55] of the reaction was reported to be either second, first or zero, depending on the glass surface. For a given glass surface, either lowering the temperature or increasing the pressure of the reactants lowered the order of the reaction. The presence of water vapor served to accelerate the reaction, but baking the glass before reaction removed this influence. Therefore, it has been suggested that bromine is hydrated at the surface of the glass, and that the ethylene reacts with the bromine hydrate.

It has been pointed out that ethylene will unite with bromine in the dark at temperatures in the range 0-15°C.[56] The rate of formation of ethylene dibromide under these conditions is said to be proportional to the bromine concentration and inversely proportional to the ethylene bromide concentration. This may be expressed by the equation,

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[48] D. F. Othmer, U. S. P. 1,917,391, July 11, 1933, to Eastman Kodak Co.; *Brit. Chem. Abs.* B, 1934, 393; *Chem. Abs.*, 1933, 27, 4544.

[49] H. G. Stone, U. S. P. 1,939,237, Dec. 12, 1933, to Eastman Kodak Co.; *Chem. Abs.*, 1934, 28, 1363.

[50] J. P. Burke, U. S. P. 2,010,426, Aug. 6, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 6246.

[51] French P. 753,890, 1933, to Fabrication francaise de produits du lait; *Chem. Abs.*, 1934, 28, 1168.

[52] S. Hamai, *Bull. Chem. Soc. Japan*, 1934, 9, 542; *Brit. Chem. Abs.* A, 1935, 325; *Chem. Abs.*, 1935, 29, 1771.

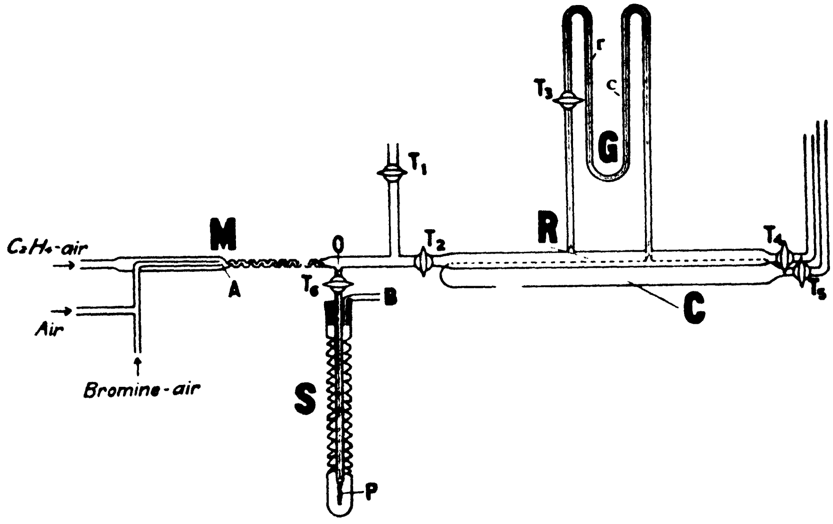
[53] The reaction was said to take place on the surface of the reaction chamber.

[54] *Cf.* Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[55] A first order reaction is one in which the rate of decomposition of the original reactant at any time is proportional to its concentration at that time. In a second order reaction, with one reactant, the rate is proportional to the square of its concentration, and with two reactants, the rate is proportional to the product of their concentrations. A reaction of zero order is one in which the rate of reaction is independent of the concentrations of the reacting substances.

$$\frac{d[C_2H_4Br_2]}{dt} = k\frac{[Br_2]}{[C_2H_4Br_2]}$$

where t is the time and k the velocity constant.



Courtesy Journal of American Chemical Society

FIG. 130.—Apparatus for Bromination of Ethylene. (T. D. Stewart and K. R. Edlund)

A. Mixing tube
B. Exit from sampling tube
C. Reaction tube
G. Manometer
M. Baffled tube
O. Coupling
P. Coil of platinum wire
R. Reaction tube
S. Sampling tube
T. Stopcocks
r, c. Arms of manometer

A mechanism has been proposed by Ogg[57] for the addition of bromine to an ethylenic linkage, when interaction is effected in the dark, at temperatures between 0° and 20°C. and in aqueous solution. Combination is stated to take place in two stages.

$$Br^- + RCH{=}CHR \longrightarrow RCHBr{-}C^-HR$$
$$RCHBr{-}C^-HR + Br{-}Br \longrightarrow RCHBr{-}CBrHR + Br^-$$

where R represents an alkyl group or a hydrogen atom. That is, the addition is catalyzed by a halide ion, and the intermediate is a carbanion. The latter is reported to have a stable configuration, and hence stereochemically[58] different products should result from *cis* and *trans* isomers. Further explanation is stated to be afforded of the generally observed *trans* addition of halogens to ethylenic linkages. Thus, the first reaction above is regarded as a substitution of the halide ion with one of the electron pair bonds of the ethylenic linkage. This stage is said to be attended by optical inversion[59] of the intermediate carbanion to the *trans* form. The carbanion thus has a *trans* configuration, and since no configuration change occurs in the second stage of the addition, the final product, it is pointed out, should be *trans*.

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[56] S. Mitsukuri, S. Kinumaki and T. Asaoka, *J. Chem. Soc. Japan*, 1933, **54**, 1061; *Chem. Abs.*, 1934, **28**, 957.

[57] R. A. Ogg, Jr., *J.A.C.S.*, 1935, **57**, 2727; *Brit. Chem. Abs.* **A**, 1936, 310; *J Inst. Pet. Tech.*, 1936, **22**, 87A; *Chem. Abs.*, 1936, **30**, 1734.

[58] These products rotate the plane of polarized light in opposite directions.

The effect of catalysts upon the rate of addition of bromine to ethylene has been investigated.[60] The union of bromine and ethylene was accomplished by mixing solutions of these reagents, both in dichloromethane at 18°C., in the dark. Hydrogen bromide was employed as catalyst in some of the experiments. The interaction was reported to be autocatalyzed when no hydrogen bromide is present. The course of the reaction was followed by withdrawing samples at definite intervals and placing them in a solution of potassium iodide. Unreacted bromine replaced the iodine, which was then determined by titration with sodium thiosulphate. A comparison of the results obtained with and without catalysts is shown in Table 111.

TABLE 111.—*Autocatalytic and Catalytic Bromination of Ethylene.*

Autocatalytic reaction at 18°C.		Catalyzed reaction at 18°C.	
Conc. of C_2H_4 = 0.0101M		Conc. of C_2H_4 = 0.0275M	
Conc. of Br_2 = 0.100M		Conc. of Br_2 = 0.0351M	
Time, Min.	C_2H_4 Reacted, %	Time, Min.	C_2H_4 Reacted, %
0.7	0.0	0.7	0.0
4.0	0.0	2.0	0.0
11.0	19.2	4.0; HBr added =	0.0001M
30.0	46.8	5.0	37.3
		7.0	58.8
		10.0	74.5
		30.0	98.0

In one method advocated for the production of ethylene dibromide, the latter compound is employed as a promoter.[61] For example, ethylene is treated with a dilute aqueous solution of bromine and the mixture conducted through a tower. Ethylene dibromide is forced through the tower countercurrent to the reactants

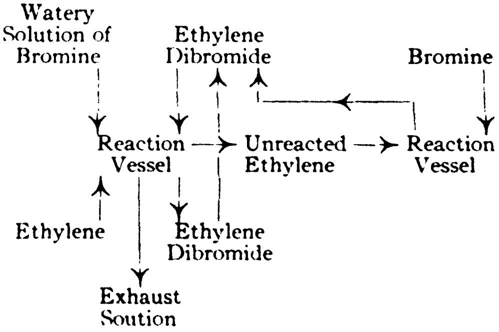

FIG. 131. Flow Chart for Bromination of Ethylene. (O. Kaselitz)

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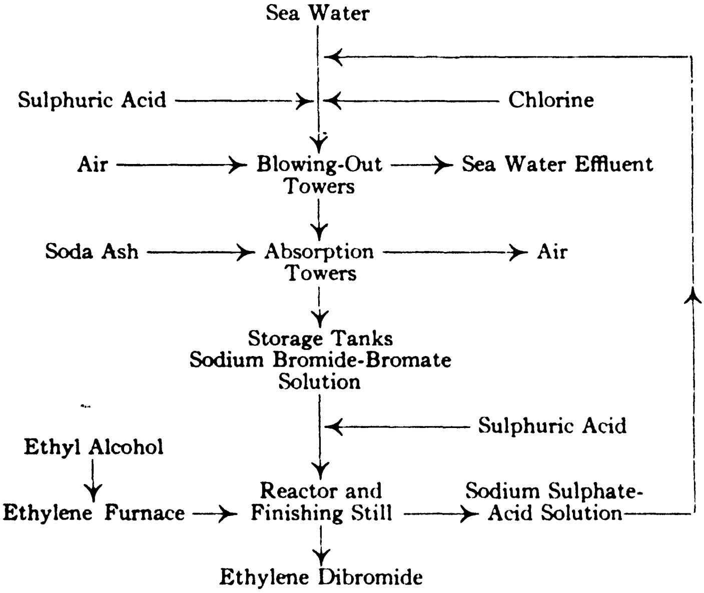
[59] A reversible isomeric change of a substance which rotates the plane of polarized light to the right into one which rotates the plane to the left.

[60] S. V. Anantakrishnan and C. K. Ingold, *J.C.S.*, **1935**, 984; *Chem. Abs.*, 1935, **29**, 6566; *Brit. Chem. Abs.* **A**, 1935, 1103. *Cf.* Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[61] O. Kaselitz, U. S. P. 1,932,590, Oct. 31, 1933; *Chem. Abs.*, 1934, **28**, 480.

(see Fig. 131). In this manner the formation of a high yield of ethylene bromide is said to be facilitated. Bromine which is in excess may be separated from the products and returned to the reaction zone.

It is interesting to note that ethylene dibromide has been manufactured with bromine extracted from sea water.[62] The latter is acidified with sulphuric acid until a pH of 3.5 has been reached. Chlorine is then added to the water to liberate bromine. To extract the bromine, a current of air is forced through the sea water. All bromine blown out of the water is afterwards absorbed in aqueous sodium carbonate, forming a mixture of sodium bromide and sodium bromate. The mixture is then acidified with sulphuric acid to liberate bromine. The latter, after being extracted, is liquefied and mixed with ethylene at temperatures between 0° and 20°C. A yield of 95 per cent of the theoretical amount of dibromide is reported to be secured.



Courtesy Dow Chemical Company

FIG. 132.—Flow Sheet for Making Ethylene Dibromide with Bromine Extracted from Sea Water.

REACTIONS OF ETHYLENE DIBROMIDE

The loss of one molecule of hydrogen bromide from ethylene dibromide leads to vinyl bromide, $CH_2{=}CHBr$. To accomplish this change it has been suggested that the products of the interaction between bromine and ethylene be heated above the boiling point of the dibromide (131.5°C.) and conducted into an alcohol solution of potassium hydroxide. The resulting vinyl bromide, which boils at 15.8°C., may be distilled from the products.[63]

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[62] L. C. Stewart, *Ind. Eng. Chem.*, 1934, **26**, 361; *Brit. Chem. Abs.* **B**, 1934, 497; *Chem. Abs.*, 1934, **28**, 3189.

[63] French P. 751,970, 1933, to La soc. anon. des ateliers de constructions mécaniques Escher Wyss; *Chem. Abs.*, 1934, **28**, 783.

The preparation of diaryl ethers of ethylene glycol from ethylene dibromide has been described.[64] For example, ethylene glycol diphenyl ether is said to be furnished by the reaction between ethylene dibromide and potassium phenolate. A mixture of 0.2 mole of phenol and 0.2 mole of potassium hydroxide was dissolved in ethanol and 25 g. of ethylene bromide incorporated. The solution was then heated under a reflux condenser for 2 hours. On cooling and filtering, crystals of ethylene glycol diphenyl ether and potassium bromide were said to be furnished. The latter compound was removed by taking advantage of its relative solubility in water as compared to the ether. The yield of ether was reported to be rather low, possibly in consequence of the formation of vinyl bromide from ethylene dibromide and the alcoholic potassium hydroxide which were employed.

Ethylene dibromide and arsenious oxide will unite to produce a number of compounds the nature of which depends upon the reaction conditions. Backer and Bolt[65] point out that combination of dibromide and arsenious oxide may be effected in aqueous caustic soda, the mixture being heated under a reflux condenser. The solution is then acidified and barium hydroxide added to furnish the barium salt of ethylene diarsonic acid, $(CH_2AsO_3Ba)_2$. When an ice-salt bath was substituted in place of heating, acetylene was said to comprise 75 per cent of the yield. In the second procedure, vinyl bromide was stated to be obtained if the arsenious oxide solution was added to the dibromide dropwise rather than by a single operation.

The action of magnesium upon ethylene dibromide was investigated to determine the possibility of forming a Grignard reagent containing two atoms of this metal.[66] The dibromide and the metal were dissolved in dry ether at 5-15°C. It was reported that, under these conditions, the only substances secured were ethylene and magnesium bromide dietherate, with a trace, at most, of a Grignard compound.

It is interesting to note that a mixture of 1 part of methyl bromide, 1 part of ethylene dibromide and 4 parts of liquid carbon dioxide has been suggested as a fire extinguisher.[67]

ETHYLENE DI-IODIDE

Apparently, little information is available upon the formation of ethylene di-iodide from ethylene and iodine. A possible explanation of this phenomenon may be the fact that the di-iodide has not yet been used industrially to as large an extent as have the corresponding dibromide and dichloride.

Among the methods which have been suggested for the production of this iodide are, the introduction of ethylene into a paste composed of iodine and alcohol, and the combination of the olefin and halogen in diffused sunlight in the cold, or in the dark when warmed.[67a]

It has been stated that ethylene di-iodide is formed rapidly when solutions of ethylene and iodine in carbon tetrachloride are exposed to red light.[68] A tungsten lamp having maximum transmission at a wave length of 700 mμ was used to energize the reactants. Solutions containing iodine were thoroughly shaken in a glass apparatus at 25°C. under a constant pressure of ethylene. All air was removed previously from the system by evacuation, and the solution was then frozen with a carbon dioxide-alcohol mixture. The rate of disappearance of iodine was determined by amount of light absorbed. No measurable dark reaction was found to take place over a period of 36 hours. The rate of addition under the influence of light was said to be dependent upon the pressure of the ethylene; further, the rate declined with decreasing concentration of the halogen. It was concluded that since the efficiency of formation of iodine atoms from activated iodine molecules may be small at 700 mμ, the observed photoiodination at this wave length may possibly proceed through the action of excited iodine molecules.

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[64] A. C. Cope, *J.A.C.S.*, 1935, **57**, 572; *Brit. Chem. Abs.* **A**, 1935, 614; *Chem. Abs.*, 1935, **29**, 2947.

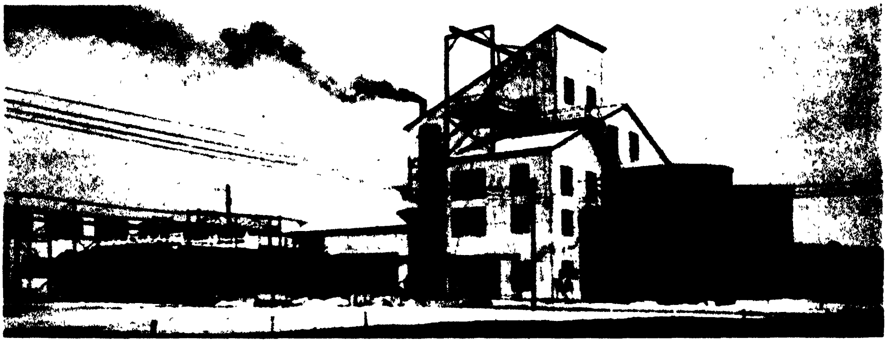
[65] H. J. Backer and C. C. Bolt, *Rec. trav. chim.*, 1935, **54**, 47; *Chem. Abs.*, 1935, **29**, 2507; *Brit. Chem. Abs.* **A**, 1935, 333.

[66] C. L. Tseng and F. M. Fam, *Science Quart. Natl. Univ. Peking*, 1934, **4**, 1; *Brit. Chem. Abs.* **A**, 1934, 508; *Chem. Abs.*, 1934, **28**, 4376.

[67] French P. 801,720 1936, to Minimax A. G.; *Chem. Abs.*, 1937, **31**, 488.

[67a] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[68] R. E. DeRight and E. O. Wiig, *J.A.C.S.*, 1936, **58**, 693; *Chem. Abs.*, 1936, **30**, 3327; *Brit. Chem. Abs.* **A**, 1936, 688.



Courtesy Dow Chemical Company

FIG. 133.—Plant for Manufacture of Ethylene Dibromide.

THE DIHALIDES OF PROPENE

Propene Dichloride. Mention has been made, in the section on ethylene dichloride, of the relatively greater velocity of the addition of chlorine to propene than to ethylene. The difference in the reaction rates has been utilized in the fractional chlorination of cracking gas.[69] The process was effected in two stages, the first resulting in the formation of propene dichloride, the second in ethylene dichloride. Two iron towers, packed with turnings of the same metal, were connected through a tube. The mixture of olefin gases was introduced into the first tower which contained chlorine at a temperature of —4°C. In this manner propene dichloride was quickly formed and separated as a liquid while the ethylene was conducted to the second tower where chlorination of this hydrocarbon was effected. The yield of propene derivatives was reported to consist of 85 per cent of propene dichloride and 15 per cent of trichloropropane.

The use of liquid solvents with and without catalysts for the production of propene dichloride has been advocated. In one procedure, propene is reacted with the halogen in the presence of a mixture of tri- and tetrachloropropane.[70] The temperature is maintained at 5°C. and the pressure at 1 atmosphere. The yield of dichloride is stated to be 76 per cent of theoretical. With solvents, such as the ones just mentioned, catalysts consisting of the chlorides of antimony, bismuth, iodine, phosphorus, sulphur, tin or manganese are said to be effective.[71] The chlorine and olefin, at 20°C. and 1 atmosphere pressure, are conducted simultaneously into the liquid containing the catalyst.

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[69] A. F. Dobryanskii, R. A. Gutner and M. K. Shchigel'skaya, *J. Applied Chem. (U.S.S.R.)*, 1933, 6, 1133; *Brit. Chem. Abs.* B, 1934, 228; *Chem. Abs.*, 1934, **28**, 4877; *J. Inst. Pet. Tech.*, 1934, **20**, 616A.

[70] M. Berliner, U. S. P. 2,022,616, Nov. 26, 1935, to Texas Co.; *Chem. Abs.*, 1936, **30**, 730.

The solvent properties of propene dichloride are similar to those of the corresponding ethylene compound. Thus, propene dichloride mixed with *o*-dichlorobenzene[72] or ethylene glycol monoethyl ether[73] is used to effect the separation of wax from lubricating oils. These mixtures are said to have complete solvent action on the oil and practically none on the wax at temperatures ranging from —10 to —22°C. A mixture of 90 per cent of propene dichloride and 10 per cent of methanol is stated to be an effective solvent for cellulose acetopropionate which has been slightly hydrolyzed.[74] Also, the dihalide has been recommended as a selective solvent for removing vinyl resinous materials from cellulose acetate.[75] At a temperature of 20°C. and a contact time of 15 minutes, propene dichloride is reported to dissolve only the vinyl resin, leaving the cellulose acetate unaffected.

Propene dichloride will form azeotropic mixtures with water and may be used for the dehydration of acetic or propionic acid.[76] The dihalide is conducted into a fractionating column near the top while the aqueous acid is introduced at the middle of the same column. The azeotropic mixture distills off, leaving a residue of the anhydrous acid.

Among the uses suggested for propene dichloride is included the preparation of insecticidal compositions. Also, the dihalide has been recommended as a paint remover. In the first case, a 9:1 mixture of propene dichloride and carbon tetrachloride is employed.[77] In the second, *o*-dichlorobenzene and propene dichloride together with small proportions of acetone, benzene and carbon tetrachloride are recommended.[78]

Propene dichloride reacts with sodium cyanide to yield a dinitrile (hydrolyzable to methyl succinic acid) and with aqueous sodium carbonate to give propene glycol.[79] Also, the dihalide may be treated with ammonia to furnish propenediamine. In the latter instance, the olefin dihalide and aqueous ammonia are heated to 120-300°C. The ratio of water to ammonia is suggested as 7:1 by volume.[80]

An attempt has been made to prepare 1,2,3-trichloropropane, $CHCl(CH_2Cl)_2$, by the further chlorination of propene dichloride.[81] Catalysts consisting of calcium and barium chloride, calcium and magnesium oxide, and calcium hydroxide were used in separate experiments. It was found that in the presence or absence of these catalysts, chlorination of propene dichloride leads to the formation of a complex mixture containing mainly 1,1,2-trichloropropane, while 1,2,3-trichloropropane was obtained in a contaminated state and in relatively small quantities. When heated with these catalysts without the addition of chlorine, the dichloride furnishes 1-chloropropene-1 and propadiene ($H_2C{=}C{=}CH_2$) but no allyl chloride from which glycerol might be secured.

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[71] British P. 425,061, 1935, to I. G. Farbenind. A.-G.; *Brit Chem. Abs.* **B**, 1935, 618; *Chem. Abs.*, 1935, **29**, 5127. French P. 770,943, 1934; *Chem. Abs.*, 1935, **29**, 817.

[72] B. Y McCarty and W. E. Skelton, U. S. P. 1,995,153, March 19, 1935, to Texas Co.; *Chem. Abs.*, 1935, **29**, 3149; *Brit. Chem. Abs* **B**, 1936, 260.

[73] B. Y. McCarty and W. E. Skelton, U. S. P. 2,027,346, Jan. 7, 1936, to Texas Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 161A; *Chem. Abs.*, 1936, **30**, 1553.

[74] French P 760,638, 1934, to Kodak-Pathé; *Chem. Abs*, 1934, **28**, 4191.

[75] L. E. Branchen, U. S. P. 1,964,191, June 26, 1934, one-half each to Carbide and Carbon Chemicals Corp. and Eastman Kodak Co.; *Brit. Chem. Abs.* **B**, 1935, 350; *Chem. Abs.*, 1934, **28**, 5236.

[76] W. W. Hartman, U. S. P. 1 908,240, May 9, 1933, to Eastman Kodak Co; *Brit. Chem. Abs.* **B**, 1934, 86; *Chem. Abs*, 1933, **27**, 3723.

[77] C. B. Dribble, *J. Econ. Entom.*, 1933, **26**, 893; *Brit. Chem. Abs.* **B**, 1933, 1074. E. I. McDaniel, *Mich Agr. Expt. Sta., Quart. Bull.*, 1933, **16**, 13; *Brit. Chem. Abs.* **B**, 1933, 1053; *Chem. Abs.*, 1934, **28**, 333.

[78] L. E. Mills and S. W. Putnam, U. S. P. 1,938,714, Dec. 12, 1933, to Dow Chemical Co.; *Chem. Abs.*, 1934, **28**, 1488, *Brit. Chem. Abs.* **B**, 1934, 896.

[79] *Cf.* Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, **1934**.

[80] N. M. Mnookin, U. S. P. 2,049,467, Aug. 4, 1936; *Chem. Abs.*, 1936, **30**, 6389.

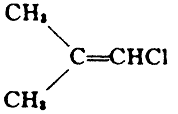
[81] A. L. Klebanskii and A. S. Vol'kenshtein, *J. Applied Chem.* (*U.S.S.R.*), 1935, **8**, 106; *Brit. Chem. Abs.* **A**, 1935, 959; *Chem. Abs.*, 1935, **29**, 6879. For a discussion of the preparation of glycerol trichlorohydrin and glycerol from propene dichloride, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

Propene Dibromide. This dibromide may be produced by passing propene into cooled bromine (or bromine water) or by the addition of dilute hydrobromic acid to allyl bromide.[82] On treatment with alcoholic potash, propene dibromide gives rise to a mixture of two isomeric bromopropenes, and on continued treatment a mixture of methylacetylene and propadiene (allene) is obtained.

A comparison of the rates of bromination of propene and ethylene was conducted by Anantakrishnan and Ingold.[83] Experiments were carried out at —78°C. with both reactants in methylene chloride solution and with all light excluded from the reaction zone. Hydrogen bromide was added to mask any autocatalytic effect. In the method a mixture of propene and ethylene was admixed with an amount of bromine insufficient to completely halogenate both compounds. The ratio of the rate constants of the simultaneous reactions was calculated from the composition of the mixture of dibromides formed after complete absorption of all of the bromine. It was reported that the ratios thus obtained are insensitive to the concentrations of the reactants, to the concentration of the hydrogen bromide catalyst, and within considerable limits (from —78 to —35°C.) to a change of temperature. Assuming that the value of the reaction rate for ethylene and bromine is 1, the reaction rate for propene and bromine was stated to be 2, or, the addition of bromine to propene proceeds twice as rapidly as the bromination of ethylene.

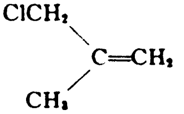
DIHALIDES OF THE BUTENES

Butene Dichloride. The action of chlorine on butene-1 and butene-2 is reported to lead to the production of the dichlorides of these two olefins in the normal way. However, in the case of isobutene, the product is not isobutene dichloride but a mixture of two isomeric chlorobutenes having the configurations:



$(CH_3)_2C{=}CHCl$

and



$(ClCH_2)(CH_3)C{=}CH_2$

Isobutene dichloride, initially formed in this reaction, undergoes immediate decomposition with elimination of hydrogen chloride to yield chlorobutenes. From these data a rather general rule has been drawn, stating that olefins which combine very readily with mineral acids yield monochloroolefins, and those which do not combine readily with mineral acids give rise to the normal addition products on treatment with chlorine.[84]

Butene dichloride has been prepared by the action of chlorine on butene-1 in the cold and in the presence of diffused daylight.[85] Butene-2 may be utilized to furnish a butene dichloride (2,3-dichlorobutane) by combining the former substance with chlorine gas at low temperatures (—10°C.).[86] Under these conditions the yield of butene dichloride is said to be 60 per cent of the theoretical.[87] The dihalide boils in the range 114-120°C. and has d_{20}^{20} 1.116.

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[82] Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, 1934.

[83] S. V. Anantakrishnan and C. K. Ingold. *J.C.S.*, 1935, 1396; *Chem. Abs.*, 1936, 30, 1733; *Brit. Chem. Abs.* A, 1935, 1465.

[84] *Cf.* Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, 1934.

[85] E. Puchot, *Ann. chim. phys.*, 1883, 28 (5), 507; *J.C.S.*, 1884, 46, 166; *Chem. Zentr.*, 1883, 482.

[86] B. A. Kazanskii and I. A. Rafilzon, *Sintet. Kauchuk*, 1934, No. 1, 31; *Chem. Abs.*, 1935, 29, 3297; *Brit. Chem. Abs.* A, 1935, 1480.

Also, it has been reported that butene dichloride is a by-product in the preparation of butene chlorohydrin from butene-2 and chlorourea ($NH_2CONHCl$). Reaction is effected at 15-17°C. in the presence of cupric chloride. The formation of the dichloride is favored by an increase in the acidity of the reaction mixture and ranges between 61 per cent (in 5 per cent hydrochloric acid) to 20 per cent (in 5 per cent acetic acid).[88] As a possible explanation of the observed phenomena it was stated that chlorourea undergoes two simultaneous reactions:

$$NH_2CONHCl + H_2O \longrightarrow HClO + CO(NH)_2$$
$$NH_2CONHCl + HCl \longrightarrow Cl_2 + CO(NH_2)_2$$

Hypochlorous acid combines with butene-2 to furnish butene chlorohydrin, while chlorine adds to the olefin producing butene dichloride:

$$CH_3CH{=}CHCH_3 + HClO \longrightarrow CH_3CHOHCHClCH_3$$
$$CH_3CH{=}CHCH_3 + Cl_2 \longrightarrow CH_3CHClCHClCH_3$$

Also, this olefin dichloride is reported to be secured in 30 per cent yield during the manufacture of the ethyl or methyl ether of butene chlorohydrin. Chlorine gas is conducted into a suspension of powdered sodium hydroxide in ethanol or methanol at a temperature of —5°C. Butene-2 is then added in small quantities to the reaction mixture.[89]

The relatively greater speed of chlorination of a tertiary carbon atom as compared to a secondary or primary carbon atom[90] has been utilized to effect selective chlorination. Thus, a mixture of isobutene (1,1-dimethylethylene) and secondary olefins from cracking gas may be treated with an amount of chlorine insufficient for complete halogenation of all the unsaturated hydrocarbons present. The reaction is carried out at low temperatures (0-60°C.) in the dark and in the absence of moisture. In this manner, 70 per cent of the theoretical amount of 1-chloro-2-methylpropene-2 ($CH_2ClCH_3C{=}CH_2$) and 1-chloro-2-methylpropene-1 ($CH_3CH_3C{=}CHCl$), based on the chlorine input, are said to be obtained.[91] Selective halogenation is also reported to be accomplished by the presence of oxygen in the reaction zone.[92] This substance, it is stated, will inhibit substitution reactions but will not affect addition. For example, a mixture of 56 per cent of butene-2 and 43.4 per cent of normal butane was chlorinated in total darkness. The procedure consisted of placing the hydrocarbons under a reflux condenser and conducting chlorine gas into this reaction zone at the rate of 120 g. per hour for a period of 10 hours. The temperature was maintained between 15° and 20°C., and a small amount of air was recycled in a closed system through the reaction flask. At the end of the reaction period no loss in the volume of air was detected, and the halogenated products were said to consist almost exclusively of butene dichloride. Further, substitution of hydrogen in isobutene by chlorine is said to be favored by atomizing this liquid and mixing it with chlorine gas at low temperatures (0°C.) and in the presence of actinic light. Carbon tetrachloride is incorporated in the reaction zone to carry off the heat furnished by the reaction.[93]

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[87] V. S. Batalin and P. G. Ugryumov, *Sintet. Kauchuk*, **1936**, No. 6, 8; *Chem. Abs.*, 1936, **30**, 6701.

[88] M. V. Likhosherstov and S. V. Alekseev, *J. Gen. Chem.* (*U.S.S.R.*), 1933, **3**, 927; *Brit. Chem. Abs.* **A**, 1934, 509; *Chem. Abs.*, 1934, **28**, 3053.

[89] M. V. Likhosherstov and A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 1348; *Chem. Abs.*, 1936, **30**, 2174; *Brit. Chem. Abs.* **A**, 1936, 453. *Cf.* M. V. Likhosherstov and S. V. Alekseev, *J. Applied Chem.* (*U.S.S.R.*), 1935, **8**, 1226; *Chem. Abs.*, 1936, **30**, 5556; *Brit. Chem. Abs.* **B**, 1936, 181.

[90] See Chapter 30.

[91] R. M. Deanesly, U. S. P. 2,010,389, Aug. 6, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 6245.

[92] R. M. Deanesly, U. S. P. 1,952,122, March 27, 1934, to Shell Development Co.; *Brit. Chem. Abs.* **B**, 1935, 138; *Chem. Abs.*, 1934, **28**, 3422. Canadian P. 338,210 and 338,211, 1933; *Chem. Abs.*, 1934, **28**, 1714, 1713. British P. 399,991, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 1714; *Brit. Chem. Abs.* **B**, 1933, 1046. British P. 402,928, 1934; *Brit. Chem. Abs.* **B**, 1934, 266. French P. 776,069, 1935; *Chem. Abs.*, 1935, **29**, 3349.

REACTIONS AND USES OF BUTENE DICHLORIDE

The removal of two molecules of hydrogen chloride from butene-2 dichloride (2,3-dichlorobutane) leads to the formation of 1,3-butadiene. In one process, the dihalide was passed through an electric oven at temperatures between 360° and 400°C. Various contact agents were employed, including barium and nickel chloride and aluminum oxide.[94] It was pointed out that barium chloride was the most efficient of the three, a 40 per cent yield of diolefin being obtained. With the others the highest amount of butadiene procured was 15 per cent. Butene dichloride may be further halogenated in the cold in the presence of direct sunlight to furnish hexachlorobutane.[95] If the temperature is raised above 35°C. it is said that two atoms of hydrogen are eliminated from the hexachlorobutane, resulting in hexachlorobutene-2. Alcoholic potassium hydroxide also interacts with the hexachlorobutane, splitting off four molecules of hydrogen chloride to give dichlorodiacetylene, $ClC{\equiv}C{-}C{\equiv}CCl$, an unstable liquid.[96]

One of the uses for which butene-2 dichloride has been recommended is as a solvent, particularly for fats and resins. It may be employed also as a liquid medium in the chlorination of hydrocarbons.[97]

BUTENE DIBROMIDE

The bromination of butene-1 can be accomplished by passage of the olefin into a cooled, aqueous solution of bromine. The product boils at 166.3°C. at 760 mm., melts at —65.4°C. and has d_4^{15} 1.8021.[98] Butene-2 dibromide, existing in several stereoisomeric forms, may be prepared by the same method as butene-1. The ease with which bromine adds to butenes is sometimes utilized in analyzing mixtures of the isomers of this olefin.[99] The mixture is converted to dihalides by treatment with bromine. The resulting substances are then fractionated and their reaction rate with potassium iodide determined.

Young and Winstein[100] distilled a mixture of butene dibromides at 210-230°C. at 760 mm. to determine the extent of isomerization of the dihalides at those temperatures. They reported that the original material had n_D^{25} 1.5118, d_4^{25} 1.7835 and reaction rate constant with potassium iodide, 0.0600. The products obtained from the distillation were said to have n_D^{25} 1.5118, d_4^{25} 1.7828 and reaction rate constant 0.0598. Traces of decomposition due to the loss of hydrogen bromide were ascribed as the cause of the slight change in density, but it was concluded that no appreciable change in properties occurs upon distillation and, therefore, that this analytical method was reliable.

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[93] R. M. Deanesly and G. Hearne, U. S. P. 2,031,938, Feb. 25, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 2199. French P. 761,614, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 4066. German P. 613,121, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 381A; *Chem. Abs.*, 1935, **29**, 5456. British P. 418,043, 1934; *Brit. Chem. Abs.* **B**, 1935, 13; *J. Inst. Pet. Tech.*, 1935, **21**, 28A; *Chem. Abs.*, 1935, **29**, 1430.

[94] B. A. Kazanskii and I. A. Rafilzon, *Sintet. Kauchuk*, **1934**, No. 1, 31; *Chem. Abs.*, 1935, **29**, 3297; *Brit. Chem. Abs.* **A**, 1935, 1480.

[95] E. Puchot, *Ann. chim. phys.*, 1883, **28** (5), 507; *Chem. Zentr.*, **1883**, 482; *J.C.S.*, 1884, **46**, 166.

[96] For a description of dihalogenodiacetylenes, see F. Straus, L. Kollek and H. Hauptmann, *Ber.*, 1930, **63**, 1886; *Chem. Abs.*, 1931, **25**, 73; *Brit. Chem. Abs.* **A**, 1930, 1158.

[97] M. V. Likhosherstov, S. V. Alekseev and T. V. Shalaeva, *J. Chem. Ind.* (*Moscow*), 1935, **12**, 705; *Chem. Abs.*, 1935, **29**, 8174; *Brit. Chem. Abs.* **B**, 1936, 10.

[98] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[99] See Chapter 49.

[100] W. G. Young and S. Winstein, *J.A.C.S.*, 1936, **58**, 102; *Brit. Chem. Abs.* **A**, 1936, 310; *J. Inst. Pet. Tech.*, 1936, **22**, 203A; *Chem. Abs.*, 1936, **30**, 2136.

In preparing ethyl propiolic acid, $C_2H_5C{\equiv}CCOOH$, the following method was employed.[101] A mixture of 85 g. of powdered sodium amide and 250 cc. of anhydrous kerosene was incorporated with 94 g. of butene-1 dibromide. The temperature was maintained at 145°C. for a period of 2 hours. At the end of that time 250 cc. of ether were added to the reactants, and a stream of dry carbon dioxide gas bubbled through the solution. Ethyl propiolic acid was precipitated in crystalline form by the latter reagent. The crystals were filtered from the solution, dissolved in water and extracted with ether. A yield of 46 per cent of the theoretical amount of acid is stated to be obtained by this method.

BUTENE DI-IODIDE

Forbes and Nelson[102] point out that iodine will react with butene-1 in dichloromethane or chloroform solution in the presence of actinic light. Solutions containing equimolecular quantities of butene-1 and iodine were placed in the solvents mentioned above and illuminated through 10 cm. of water by incandescent lamps. It was observed that 90 per cent of the iodine disappeared at —60 to —90°C. when dichloromethane was the liquid medium, and that 98 per cent disappeared at —60 to —70°C. if chloroform was the solvent. Further, the halogen was said to be unaffected photochemically by either chlorinated hydrocarbon. Such solutions of photoiodinated butene were illuminated in quartz flasks by a spark passing between tungsten-steel electrodes. In each instance iodine was evolved quantitatively within an hour as determined by titration with sodium thiosulphate at definite time intervals. Another sample of iodinated butene, when kept at 20°C. for a period of four days in the absence of light, had evolved 84 per cent of the iodine which had been chemically combined with butene. The conclusion was drawn that the reaction between the olefin and halogen proceeds to the formation of butene-1 di-iodide in the presence of visible light, and to the decomposition of the dihalide under the influence of ultraviolet light or heat.

DICHLORIDES OF THE AMYLENES

According to Hell and Wilderman[103] interaction of chlorine with amylene-1 is exothermic. They recommend that addition of halogen to this olefin be effected at —17°C. in the presence of actinic light. A mixture of chlorinated derivatives was said to be secured under these conditions. The substances obtained were 31 parts of monochloropentene, 44 parts of amylene-1 dichloride, 10 parts of liquid trichloropentane, and a trace of tetrachloropentane. The first boils at 92-93°C., the second at 130-133°C., and the third at 174-180°C., all under a pressure of 760 mm.

Phosphorus pentachloride was found to interact with amylene-1 to form amylene-1 dichloride, monochloropentene and trichloropentane.[104] It was pointed out that if union of the two reactants was brought about at low temperatures (1 to 5°C.) and the products poured on to ice as soon as the reaction was completed, only pentene-1 dichloride and monochloropentene would be obtained. If, however, the temperature rises above the upper limit mentioned, (above 5°C.) a mixture of the latter substances together with trichloropentane is produced. The latter compound was said to be secured by the displacement of hydrogen in amylene-1 dichloride and by the addition of chlorine to monochloropentene. It was thought that the presence of chloroolefin was due to the heat developed in the reaction, which caused the elimination of a molecule of hydrogen chloride from the amylene-1 dichloride first formed. Further, it was concluded, from the relative proportions of the products, that amylene-1 dichloride loses hydrogen chloride more readily than it takes up another atom of chlorine by substitution, and that chlorine acts more easily on amylene-1 than on monochloropentene.

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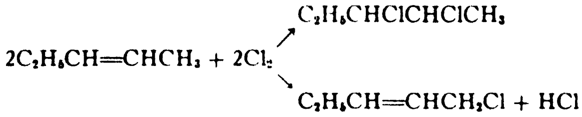
[101] A. E. Favorskii and V. O. Mokhnach. *Bull. Far Eastern Branch Acad. Sci. U.S.S.R.*, 1934, **9**, 3; *Chem. Abs.*, 1935, **29**, 3981. *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 1668; *Brit. Chem. Abs.* **A**, 1936, 705.

[102] G. S. Forbes and A. F. Nelson, *J.A.C.S.*, 1936, **58**, 182; *Brit. Chem. Abs.* **A**, 1936, 310; *Chem. Abs.*, 1936, **30**, 1734.

[103] C. Hell and M. Wilderman, *Ber.*, 1891, **24**, 216; *J.C.S.*, 1891, **60**, 533; *Chem. Zentr.*, 1891, 1, 495.

[104] C. Hell and M. Wilderman, *loc. cit.*

The relative proportions of substitution and addition by chlorine interacting with amylene-2 have been investigated.[105] The two reactions, which may be indicated as



$$2C_2H_5CH{=}CHCH_3 + 2Cl_2 \begin{cases} \nearrow C_2H_5CHClCHClCH_3 \\ \searrow C_2H_5CH{=}CHCH_2Cl + HCl \end{cases}$$

were effected by dissolving separately known quantities of the two reagents in carbon tetrachloride and mixing the solutions at temperatures between −10.1° and 25°C. for a period of 15 seconds. Some of the results obtained in this manner are indicated in Table 112. The results are given, not in terms of reaction rates or amounts of the two chlorides, but by induction factors, which represent the ratio of the moles of chlorine producing hydrogen chloride to the moles of chlorine reacting by addition.

TABLE 112.—*The Relative Amounts of Substitution and Addition by Chlorine in Pentene-2.*

Initial Concentrations, Moles Per Liter		Induction Factor
Chlorine	Pentene-2	
0.101	0.097	1.23
0.0464	0.097	1.60-1.64
0.101	0.051	0.57
0.0464	0.051	0.88-0.93
0.00954	0.051	3.04-3.24
0.0464	0.0097	0.72-0.78

It was believed that the above data indicate that substitution was favored by a relative increase in the concentration of the olefin or by a relative decrease in the halogen concentration. The effect of a change of temperature upon the induction factor (within the range investigated) was stated to be very slight. It was also noted that the presence of water, hydrogen chloride or powdered glass produced no change in the rates of addition and substitution.

As a tentative explanation, a chain mechanism based upon competitive reactions for a common intermediate has been suggested. It may be represented as:

$$\begin{aligned} Cl_2 &\longrightarrow 2Cl \text{ (thermally)} \\ C_5H_{10} + Cl &\longrightarrow C_5H_{10}Cl \\ C_5H_{10}Cl + Cl_2 &\longrightarrow C_5H_{10}Cl_3 \\ C_5H_{10}Cl_3 &\longrightarrow C_5H_{10}Cl_2 + Cl \\ C_5H_{10} + C_5H_{10}Cl &\longrightarrow C_5H_9 + C_5H_{10} + HCl \\ C_5H_9 + Cl_2 &\longrightarrow C_5H_9Cl + Cl \end{aligned}$$

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[105] T. D. Stewart and B. Weidenbaum, *J.A.C.S.*, 1936, **58**, 98; *Brit. Chem. Abs.* **A**, 1936, 310; *Chem. Abs.*, 1936, **30**, 1733.

The action of chlorine upon trimethylethylene has been investigated.[105a] It was stated that when halogenation was effected at −17°C. in the presence or absence of calcium carbonate or sodium bicarbonate, a mixture of chlorine derivatives was obtained. The substances said to be isolated are: 2-chloro-2-ethylpropane; 2-methyl-3-chlorobutene-1; 3-chloropentene-2; 2,3-dichloro-2-methylbutane; 1,3-dichloro-2-methylbutane; 1,2,3-trichloro-2-methylbutane; 1,3-dichloro-2-chloromethylbutane; and 1,2,3-trichloro-2-chloromethylbutane. To explain this phenomenon the explanation was offered that the chlorination of trimethylethylene is accompanied by a number of parallel reactions.

1. Formation of a complex of chlorine and trimethylethylene, of which a portion stabilizes to form 2,3-dichloro-2-methylbutane while another portion splits off hydrogen chloride to furnish 2-methyl-3-chlorobutene-1.
2. Addition of hydrogen chloride both to trimethylethylene, giving 2-chloro-2-ethylpropane, and to 2-methyl-3-chlorobutene-1, yielding 2,3-dichloro-2-methylbutane and 1,3-dichloro-2-methylbutane.
3. Substitution by chlorine in 1,3-dichloro-2-methylbutane, leading to 1,2,3-trichloro-2-methylbutane and 1,3-dichloro-2-chloromethylbutane.
4. Substitution of chlorine in 1,2,3-trichloro-2-methylbutane and 1,3-dichloro-2-chloromethylbutane to furnish 1,2,3-trichloro-2-chloromethylbutane.
5. Isomerization of 2-methyl-3-chlorobutene-1 and 2,3-dichloro-2-methylbutane.

Among the uses for which amylene-1 dichloride has been advocated is the preparation of lubricating oils of low pour point by precipitation of the wax present.[106] When mixed with lubricating oil, the dihalide is reported to give to the oil a high penetrating power.[107] Also, it has been suggested that the dichloride be used to soften road-tar splashes on vehicles.[108] Further, it has been recommended that amylene dichloride be admixed with diamylamine and sodium hydroxide to furnish an insecticidal composition.[109]

AMYLENE DIBROMIDE

Bromine is said to act on amylene at −17°C. to yield amylene dibromide, tribromopentane, tetrabromopentane and isoamyl bromide.[110] The formation of monobromoamylene was believed to be inhibited to a large extent, possibly because the reaction of olefin and bromine is not as exothermic as that with chlorine. Amylene dibromide boils at 175°C. at 760 mm., tribromopentane at 118-119°C. at 12 mm., tetrabromopentane at 148-150°C. at 12 mm., and isoamyl bromide at 254°C. at 760 mm. Amylene dibromide may be further brominated at 100°C. to furnish tri- and tetrabromopentane and higher brominated derivatives. It is interesting to note that the action of bromine upon monobromoamylene in direct sunlight leads to a crystalline tribromopentane which melts at 207°C. Addition of bromine to amylene apparently differs from that of chlorine in that with the former only a trace of monohalogenated olefin is produced and that the higher brominated derivatives are obtained largely from amylene dibromide.

Reactions of Amylene Dibromide. The removal of two molecules of hydrogen bromide from amylene dibromide leads to the production of acetylenes.

[105a] D. V. Tishchenko, *J. Gen. Chem. (U.S.S.R.)*, 1936, **6**, 1116; *Chem. Abs.*, 1937, **31**, 1003.

[106] B. Y. McCarty and W. E. Skelton, U. S. P. 1,969,670, August 7, 1934, to Texas Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 540A; *Brit. Chem. Abs* **B**, 1935, 617; *Chem. Abs.*, 1934, **28**, 6297.

[107] R. R. Vallee, U. S. P. 1,926,961, Sept. 12, 1933, to Sharples Solvents Corp.; *Chem. Abs.*, 1933, **27**, 5962; *Brit. Chem. Abs.* **B**, 1934, 567.

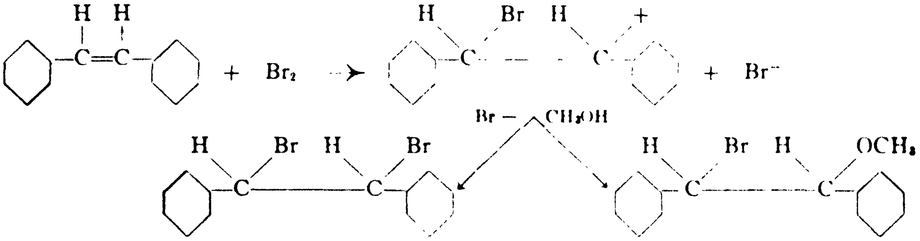
[108] R. R. Vallee, U. S. P. 1,913,647, June 13, 1933, to Sharples Solvents Corp.; *Brit. Chem. Abs.* **B**, 1934, 310; *Chem. Abs.*, 1933, **27**, 4364.

[109] M. M. Wilson, U. S. P. 2,014,077, Sept. 10, 1935, to Sharples Solvents Corp.; *Chem. Abs.*, 1935, **29**, 7572; *Brit. Chem. Abs.* **B**, 1936, 1082.

[110] C. Hell and M. Wilderman, *Ber.*, 1891, **24**, 216; *Chem. Zentr.*, 1891, 1, 495; *J.C.S.*, 1891, **60**, 1891.

For example, Hall and Bachman[111] recommend that 1 mole of 1,2-dibromopentane (amylene-1 dibromide) be dehalogenated by use of the requisite amount of potassium hydroxide suspended in a mineral oil. The three substances were heated in a distilling flask connected to a condenser, from which the portion boiling at 39.5-41.0°C. at 747 mm. was retained. This product, pentyne-1, was said to constitute 33 per cent of the theoretical amount. The residue contained monobromoamylene-1 which was converted to the pentyne by heating 1 mole of the latter under a reflux condenser for 5 hours with 3 moles of alcoholic potassium hydroxide.

Bromination of stilbene, $C_6H_5CH{=}CHC_6H_5$, has been reported by Bartlett and Tarbell.[112] Reaction was carried out at 0°C. by dissolving stilbene and bromine separately in methanol and mixing the two solutions. The products of the interaction were stilbene dibromide and stilbene methoxy bromide, so that the mechanism may be expressed as:



The rate of addition was followed by withdrawing samples from the reaction flask, diluting them with 5 times their volume of water containing potassium iodide and titrating the liberated iodine with sodium thiosulphate. The rate of bromination was reported to be diminished by bromine ions but not by hydrogen ions. Therefore, it was concluded that, though stilbene methoxy bromide, C_6H_5CHBr-$CH(OCH)_3C_6H_5$, is the main product, methyl hypobromite is not responsible for its formation. The reason for this statement was said to be the fact that bromine reacts with methanol to form methyl hypobromite, hydrogen ions and bromine ions,

$$Br_2 + CH_3OH \rightleftharpoons CH_3OBr + H^+ + Br$$

and that, if this mechanism was correct, the addition of hydrogen ions should produce the same effect upon the rate of reaction as do bromine ions. This, as was mentioned before, was not observed.

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[111] H. J. Hall and G. B. Bachman, *Ind. Eng. Chem.*, 1936, **28**, 57; *Brit. Chem. Abs.* **B**, 1936, 306; *Chem. Abs.*, 1936, **30**, 1356.

[112] P. D. Bartlett and D. S. Tarbell, *J.A.C.S.*, 1936, **58**, 466; *Chem. Abs.*, 1936, **30**, 2952; *Brit. Chem. Abs.* **A**, 1936, 600.

Chapter 21

Production, Properties and Uses of Halohydrins Derived from Simple Olefins

Comparatively little new work is available on the production of halohydrins of the simpler olefins. This is somewhat surprising, in view of the large amount of research which has been directed to the use of this class of compounds, in particular ethylene chlorohydrin, in chemical synthesis. A number of new compounds, however, some of technical importance, have been developed from the alkene chlorohydrins. An example of such is β,β'-dichloroethyl ether, which has found application in the refining of petroleum distillates, particularly lubricating oils.

On the other hand, the preparation of chlorohydrins of the butenes and higher olefinic hydrocarbons has received some attention. Also, several processes dealing with the production of halohydrins of halogenated olefins have also been described.

Ethylene Chlorohydrin

This chlorohydrin, CH_2ClCH_2OH, is made by the well-known reaction between hypochlorous acid and ethylene.[1] One procedure comprises passage of ethylene and chlorine simultaneously into water. In this instance formation of ethylene chlorohydrin can be represented by

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$
$$C_2H_4 + HOCl \longrightarrow CH_2ClCH_2OH$$

Generally, the concentration of the desired product in the aqueous medium must be kept rather low, say 6 to 8 per cent, otherwise a large proportion of ethylene dichloride may be obtained. Various proposals have been advanced for increasing the yields of chlorohydrin, as, for example, removal of hydrochloric acid (formed as a by-product) by addition of soda ash or incorporation of catalysts, such as cupric chloride or ferric chloride.

Other methods of preparation involve the use of aqueous solutions of hypochlorites, e.g., the sodium or calcium salts. In such cases hypochlorous acid is liberated by the simultaneous introduction of carbon dioxide with gaseous ethylene. The same effect (liberation of hypochlorous acid) may be accomplished also by incorporation of sodium bicarbonate in the reaction mixture. Employment of a solvent which is immiscible with the aqueous medium has been recommended. The presence of this immiscible liquid tends to remove the chlorohydrin from the water layer and thus retard its further interaction with either chlorine or hydrogen chloride.

A procedure developed by Detoeuf,[2] using N-chlorourea as the chlorinating agent, has been described by Likhosherstov and Alekseev.[3] Ethylene is passed through a 5 per cent sulphuric acid solution (at 0°C.) containing N-chlorourea, $NH_2CONHCl$, and cupric chloride. After about five hours a 60 to 70 per cent yield of ethylene chlorohydrin is secured, together with 2 to 2.5 per cent of ethylene dichloride. If additional quantities of N-chlorourea are introduced into the reaction mixture from time to time, concentrations of ethylene chlorohydrin up to 25 to 30 per cent may be produced.

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[1] For a review of the various methods for carrying out this reaction, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[2] A. Detoeuf, *Bull. soc. chim.*, 1922, **31**, 102; *Chem. Abs.*, 1922, **16**, 1395; *Brit. Chem. Abs.* **A, 1922**, 196.

Ethylene chlorohydrin is also formed by the interaction of liquid hydrogen chloride and ethylene oxide.[4]

TECHNICAL PROCESSES FOR CHLOROHYDRIN PRODUCTION

The large number of processes which have been developed may be divided into two general types: vapor-phase and liquid-phase operations.[5] The latter are based essentially on the principles mentioned previously, i.e., gaseous ethylene is passed into a liquid medium (water) containing hypochlorous acid. This acid may result from the interaction of chlorine (introduced simultaneously with ethylene) and water, or from dissolved hypochlorites and a weak acid such as carbonic or boric. Generally, the temperature is kept at 30°C. or lower. In vapor-phase methods, the olefin, hydrogen chloride and steam are reacted at temperatures of 100°C. or slightly higher. A large excess of steam is employed to prevent, insofar as possible, the formation of dihalogen derivatives of the hydrocarbon.

Kautter[6] describes an apparatus in which an excess of aliphatic olefin (at atmospheric temperature) is bubbled through an aqueous solution of free hypochlorous acid and hydrochloric acid. Alternatively, the unsaturated hydrocarbon may be passed in a countercurrent manner to a spray of continuously circulated aqueous solution of chlorine and chlorohydrin. Afterwards the chlorohydrin solution is dehydrated by distilling with a paraffin having the same number of carbon atoms as the olefin.

Among the methods used for the interaction of chlorine, water and ethylene may be noted two in which the chlorine gas is added to water in a separate container from the one where the hypochlorous acid solution is treated with olefin. In one case,[7] a mutual exchange of liquids is maintained between the absorbing fluids. In the second procedure[8] interaction takes place by circulating hypochlorous acid solution (maintained at not less than 15 per cent saturation as to chlorine) in countercurrent to the ethylene or propene gas to be absorbed. No neutralizing agent is present in the system.

A method adopted by Dreyfus[9] is to heat a di- or polyhydric alcohol with hydrochloric acid generated *in situ*. For example, monochlorohydrin may be produced by heating in an autoclave at 50° to 60°C. a mixture of glycerol, 90 per cent sulphuric acid and sodium chloride with a small amount of acetic acid as an activator. Addition of more sulphuric acid and continued heating at higher temperatures (200-250°C.) converts the chlorohydrin into the corresponding ether.

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[3] M. V. Likhoshertov and S. V. Alekseev, *J. Applied Chem. (U.S.S.R.)*, 1934, 7, 127; *Chem. Abs.*, 1935, **29**, 452; *Brit. Chem. Abs.* **B**, 1934, 567.

[4] E. Gebauer-Fuelnegg and E. Moffett, *J.A.C.S.*, 1934, **56**, 2009; *Chem. Abs.*, 1934, **28**, 6698; *Brit. Chem. Abs.* **A**, 1934, 1200.

[5] For a discussion of these, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. Also, R. Kassler, *Homicky Vistnik*, 1932, **14**, 454; *Chem. Abs.*, 1933, **27**, 5715.

[6] C. T. Kautter, U. S. P. 2,007.168, July 9, 1935, to Shell Development Co.; *Chem. Abs.*, 1935 **29**, 5459. British P. 426.519, 1935, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1935, 584; *J. Inst. Pet. Tech.*, 1935, **21**, 223A. French P. 769.404, 1934; *Chem. Abs.*, 1935, **29**, 476.

[7] French P. 799,150, 1936, to Usines de Melle (Soc. anon.); *Chem. Abs.*, 1936, **30**, 7585. British P. 458.061, 1936; *J. Inst. Pet. Tech.*, 1937, **23**, 79A.

[8] British P. 450.372, 1936, to Société Carbochimique Soc. anon.; *Chem. Abs.*, 1936, **30**, 8241; *Brit. Chem. Abs.* **B**, 1936, 972; French P. 800.662, 1936; *Chem. Abs.*, 1936, **30**, 8241.

[9] H. Dreyfus, British P. 404,938, 1932; *Brit. Chem. Abs.* **B**, 1934, 266; *Chem. Abs.*, 1934, **28**, 4432.

Another procedure[10] involves reacting chlorine and ethylene in an aqueous medium and removing the insoluble chlorinated products from the reaction mixture as they are formed. In an analogous process, addition of ammonia to the reaction mixture is advocated.[11] In this manner the hydrogen halide, formed as a by-product, is converted into ammonium chloride. Or, the hydrochloric acid may be neutralized by conversion into aluminum chloride.[12] In either case the chlorohydrin is recovered by distillation.

Under ordinary conditions of ethylene chlorohydrin production, the reaction mixture is somewhat corrosive. The problems arising from this fact have been met in various ways. A usual method, as will be apparent from the foregoing, comprises incorporation of alkali to neutralize the hydrochloric acid present. Rotshtein[13] suggested that the reaction vessel be made of wood, covered with a phenol-aldehyde resin.

Iskra[14] studied the corrosive properties of a mixture consisting of 7 to 7.5 per cent ethylene chlorohydrin, 5 to 6 per cent ethylene dichloride, 81.5 to 83.5 per cent water, some hydrochloric acid and an excess of chlorine. Lead was quickly attacked at temperatures above 20°C. as were also a large number of alloys and acid-resisting lacquers. Of the former, ferrosilicon, containing 13 to 17 per cent of silicon, gave the most promising results. The most refractory coating was shown to consist of a Haveg type resin,[15] applied as an asbestos-resin plaster on an iron surface. In this instance the resin was only slightly corroded. None of the lacquers tested gave satisfactory results.

A process for preparing alkene chlorohydrins by utilizing the action of sulphur trioxide on the corresponding dichloride is described by Isham and Spring.[16]

An alkene dichloride is treated with sulphur trioxide to obtain a chloroalkylsulphuric chloride which, hydrolyzed with water, forms a chlorohydrin. The latter may then be separated by distillation or by use of a solvent. Application of this method for production of ethylene chlorohydrin from ethylene involves the following reactions:

$$\begin{aligned} C_2H_4 + Cl_2 &\rightarrow C_2H_4Cl_2 \\ C_2H_4Cl_2 + SO_3 &\rightarrow ClC_2H_4SO_3Cl \\ ClC_2H_4SO_3Cl + 2H_2O &\rightarrow CH_2ClCH_2OH + HCl + H_2SO_4 \end{aligned}$$

The quantities of ethylene dichloride and sulphur trioxide used may vary somewhat. However, when employed in molecular proportions (or the dichloride in excess), the best yields of intermediate product with least undesirable by-products and loss of dichloride were secured.

Although the optimum reaction range for the dichloride and sulphur trioxide lies between 35° and 45° C., it was found necessary to maintain a temperature of 5° to 10°C. during the addition of the sulphur trioxide. This was accomplished by precooling the trioxide to just above its solidification point prior to mixing the reactants. In practice, the reaction mass is then removed to a vacuum still where temperature control is possible and separation of unreacted ethylene dichloride and sulphur trioxide is readily effected. After chemical equilibrium is established by holding at about 40°C., removal of a large proportion of the unused dichloride and trioxide serves to concentrate the chloroethylsulphuric chloride. It was noted that the rate of formation of this latter product was considerably increased by the use of reflux reaction between the unreacted ethylene dichloride and sulphur trioxide as these products were driven off.

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[10] French P. 785,170, 1935, to Compagnie de produits chimiques et electrometallurgiques Alais, Froges et Camargue, *Chem. Abs.*, 1936, **30**, 492.

[11] French P. 795,804, 1936, to Société Carbochimique, Soc. anon; *Chem. Abs.*, 1936, **30**, 5592. British P. 445,011, 1936; *Chem. Abs.* 1936, **30**, 6390.

[12] P. Ferrero and C. Vandendries, U. S. P. 2,056,448, Oct. 6, 1936, to Société Carbochimique, Soc. anon.; *Chem. Abs.*, 1936, **30**, 8242.

[13] A. D. Rotshtein, Russian P. 35,183, 1934, *Chem. Abs.*, 1936, **30**, 2580.

[14] E. V. Iskra, *J. Chem. Ind. (U.S.S.R.)*, 1935, **12**, 947; *Chem. Abs.*, 1936, **30**, 711; *Brit. Chem. Abs.* **B**, 1936, 201.

[15] For the preparation and uses of resins of the Haveg type, see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**, 458, et seq.

[16] R. M. Isham and O. Spring, U. S. P. 1,918,967, July 18, 1933, to Doherty Research Co.; *Chem. Abs.*, 1933, **27**, 4815; *Brit. Chem. Abs.* **B**, 1934, 393.

Hydrolysis of the crude chloroethylsulphuric chloride may be carried out in three ways:

1. By mixing with water held near 0°C. and gradually heating to about the boiling point.
2. By adding crude chloride just fast enough to allow heat of hydrolysis to hold the water at its boiling point. (This method requires especial care.)
3. By hydrolysis with cold water which takes longer but normally affords larger yields of ethylene chlorohydrin.

For complete hydrolysis vigorous agitation and the presence of a small amount of sulphuric acid are recommended.

If the hydrolysis is carried out in a distillation unit, the product may be readily recovered by fractional distillation. A constant-boiling mixture of water and ethylene chlorohydrin contains approximately 46 per cent of the latter and boils at 93-94°C. This azeotropic mixture can, in turn, be dehydrated by distillation with ethylene dichloride, which takes out the water in azeotropic mixture at 72°C. Another immiscible solvent available is butyl acetate.

The chlorohydrins of propene, butene and higher olefins may be prepared by the above process. The temperature in these cases must be maintained below 0°C. when reaction with sulphur trioxide is carried out. In addition, cold water is recommended for hydrolysis.

In another procedure,[17] halohydrins are obtained by reaction of the olefin with a tertiary alcohol ester of hypochlorous (or hypobromous) acid in the presence of water. Ethylene, for example, gives ethylene chlorohydrin and tertiary butyl alcohol when passed into a mixture of *ter*-butyl hypochlorite and water at 18 to 22°C. This method is reported equally applicable to the preparation of the chlorohydrins and bromohydrins of propene, isobutene, isoprene and cyclohexene. The tertiary alcohol esters of the hypohalous acids are prepared by passing chlorine or bromine into the aqueous alcohol containing sodium hydroxide.

An alcohol that is easily dehydrated, e.g., *ter*-butyl alcohol, can be used to prepare an alkene chlorohydrin[18] if treated in the presence of water with a hypohalogenous acid. Instead of the acid a hypohalite ester, such as butyl hypochlorite, may be used if it has an alkyl group next to the hypohalogenous acid radical.

Alkene chlorohydrins are formed along with aliphatic esters when olefin diesters of saturated aliphatic monocarboxylic acids are treated with hydrochloric acid and an alcohol.[19] For example, ethylene glycol diacetate treated with hydrochloric acid and ethyl alcohol gives ethylene chlorohydrin and ethyl acetate.

PROPERTIES AND USES OF ETHYLENE CHLOROHYDRIN

A physico-chemical study of ethylene chlorohydrin has been made by Radulescu and Muresanu.[20] Hydrolysis of this compound was found to be unimolecular, and the reaction constants at different temperatures were determined as follows:

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[17] British P. 402,880, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 2726; *Brit. Chem. Abs.* B, 1934, 267; *J. Inst. Pet. Tech.*, 1934, 20, 115A. French P. 740,350, 1932; *Chem. Abs.*, 1933, **27**, 2160. German P. 590,432, 1934; *Chem Abs.*, 1934, **28**, 2014. Dutch P. 31,306, 1933; *Chem. Abs.*, 1934, **28**, 2372.

[18] S. L. Langedijk, U. S. P. 2,046,469, July 7, 1933, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 5592.

[19] E. C. Britton, G. H. Coleman and G. V. Moore, U. S. P. 1,987,227, Jan. 8, 1935, to Dow Chemical Co.; *Chem. Abs.*, 1935, **29**, 1432; *Brit. Chem. Abs.* B, 1935, 1130.

[20] D. Radulescu and P. L. Muresanu, *Bul. soc. stiinte Cluj*, 1932, 7, 129; *Chem. Zentr.*, **1933**, **1**, 3156; *Brit. Chem. Abs.* **A**, 1933, 1271; *Chem. Abs.*, 1933, **27**, 2085.

	Reaction Constant
At 56°C.	0.0000036
At 65°C.	0.0000080
At 79°C.	0.0000408
At 99°C.	0.00029

These values were not affected by the presence of calcium chloride, sodium chloride or hydrogen chloride. Equivalent quantities of ethylene glycol and hydrogen chloride, in solutions varying in concentration from 0.2 to 2N, reacted very slowly at 99°C. to give the chlorohydrin.

Indices of refraction of ethylene chlorohydrin were found to be

At 10°C.	1.44551
At 15°C.	1.44382
At 20°C.	1.44212
At 25°C.	1.44123

Density determinations gave the following values:

At 15°C.	1.2014
At 20°C.	1.1981
At 25°C.	1.1954

Ethylene chlorohydrin has been found to possess a high degree of toxicity as an insecticide.[21] Ginsburg[22] reports, after testing the effect of a number of fumigants on codling-moth larvae, that this halohydrin was second only to liquid hydrocyanic acid in order of potency. It was observed, however, that the percentage kill was considerably reduced as the temperature was lowered. It has likewise been noted[23] that the rate of hydrolysis of starch by the enzyme, amylase, is increased by ethylene chlorohydrin; but, according to Denny,[24] the accelerating effect of this latter compound on the growth of dormant buds is not directly due to its stimulating influence on the activity of the enzyme.[25] Ethylene chlorohydrin has been suggested as a refining agent for rosin[26] to be used in the manufacture of glaze for paper. Further, it has been recommended that the chlorohydrin be employed to remove naphthenic compounds from crude petroleum.[26a]

Butene Chlorohydrins

Batalin and Ugriumov[27] have described the preparation of butene-2 chlorohydrin by two different methods. In the first, after the manner adopted by Gomberg,[28] a yield of 50 to 60 per cent in 7 to 8 per cent concentration was obtained. A modification of McElroy's[29] process proved more convenient and gave 60 to 65 per cent of the chlorohydrin and 10 to 30 per cent of the dichloride. In each case the utilization of butene-2 was 85 per cent. The product was separated from the reaction mixture by distillation with steam under reduced pressure.[30]

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[21] K. Brodersen and H. Behncke, German P 612,206, 1935, to I. G. Farbenind. A.G.; *Chem. Abs.*, 1935, **29**, 4890.

[22] J. M. Ginsburg, *J. Agric. Res.*, 1933, **46**, 1131; *Brit. Chem. Abs.* **B**, 1933, 934; *Chem. Abs.*, 1933, **27**, 5464.

[23] R. H. Clark, F. L. Fowler and P. T. Black, *Trans. Roy. Soc. Canada*, 1931, (3) **25**, 99; *Brit. Chem. Abs.* **A**, 1932, 427; *Chem. Abs.*, 1932, **26**, 2755.

[24] F. E. Denny, *Contrib. Boyce Thompson Inst.*, 1933, **5**, 441; *Brit. Chem. Abs.* **A**, 1933, 1215; *Chem. Abs.*, 1933, **27**, 5765.

[25] For the effect of this chlorohydrin on potato tubers, see L. P. Miller, *Contrib. Boyce Thompson Inst.*, 1934, **6**, 123; *Chem. Abs.*, 1934, **28**, 5853. For the action on gladiolus corms, see F. E. Denny, *Contrib. Boyce Thompson Inst.*, 1933, **5**, 435; *Chem. Abs.*, 1933, **27**, 5781; *Brit. Chem. Abs.* **B**, 1933, 1215.

[26] German P. 577,723, 1933, to Hercules Powder Co.; *Chem. Abs.*, 1934, **28**, 663.

[26a] S. W. Ferris, U. S. P. 2,072,104, March 2, 1937, to Atlantic Refining Co.

[27] V. S. Batalin and P. G. Ugriumov, *J. Gen. Chem. (U.S.S.R.)*, 1934, **4**, 871; *Chem. Abs.*, 1935, **29**, 2147; *Brit. Chem. Abs.* **A**, 1935, 62.

[28] M. Gomberg, *J.A.C.S.*, 1919, **41**, 1414; *Chem. Abs.*, 1919, **13**, 2369; *J.C.S.*, 1919, **116** (1), 567; *Brit. Chem. Abs.* **A**, 1919, 923. Essentially passage of chlorine and ethylene (in excess) into water at 10 to 12°C. until concentration of the halohydrin is 6 to 8 per cent.

[29] K. P. McElroy, U. S. P. 1,253,616, Jan. 15, 1918; *Chem. Abs.*, 1918, **12**, 703; *J.S.C.I.*, 1918, **37**, 167A. Involves the reaction of chlorine, ethylene and steam at 100°C.

The ethers of butene-2 chlorohydrin are formed when chlorine is passed into an alcoholic solution of sodium hydroxide at —5°C. while butene-2 is being gradually added.[31] Excess of chlorine (25 per cent) and of alkali (30 per cent) are necessary. The alkali chloride and unchanged alcohol may be removed from the reaction mixture by repeated washings with water and the product then dried with calcium chloride and distilled. By this procedure 60 to 70 per cent yields of the ethers can be obtained, with 25 to 35 per cent of dichlorides as by-products. The properties of the methyl, ethyl and isobutyl ethers of butene-2 chlorohydrin are given in Table 113.

TABLE 113.—*Monoalkyl Ethers of Butene-2 Chlorohydrin.*

Ether	Formula	Boiling Point	d^{15}	n_D^{15}
Methyl.........	$CH_3CHClCH(OCH_3)CH_3$	116-118°C.	1.0102	1.426
Ethyl..........	$CH_3CHClCH(OC_2H_5)CH_3$	122-126°C.	1.0002	1.424
Isobutyl........	$CH_3CHClCH[OCH_2CH(CH_3)_2]CH_3$	164-166°C.	0.9273	1.421

The preparation of isobutene chlorohydrin from *ter*-butyl hypochlorite and *ter*-butyl alcohol has been briefly discussed earlier in this chapter.[32]

CHLOROHYDRINS OF SEVERAL HIGHER OLEFINS

The formation and properties of some of the higher homologues of ethylene chlorohydrin have been described by Nilsson and Smith.[33] These workers prepared the α-dimethyl-, trimethyl-, tetramethyl- and α-diethyl-ethylene chlorohydrins and determined their rates of hydrolysis in neutral and alkaline solutions at 18°C. For a homologous series the rate in neutral solution appeared to be unaffected by the substitution of a methyl group for a hydrogen atom. However, in alkaline media, a considerable increase was observed when the same change in composition was made. These results are in accordance with Michael's[34] rule.

Godchot, Mousseron and Granger[35] synthesized a number of cyclic chlorohydrins by the action of hypochlorous acid on the corresponding cyclic olefin.

2-Chlorocyclopentanol. A mixture of the *cis* and *trans* isomers of this compound is formed when hypochlorous acid is allowed to react with cyclopentene. Some separation can be effected by careful fractionation of the product, although the *cis*-2-chlorocyclopentanol obtained (b.p. 44°C. at 15 mm.) probably contains a small proportion of 1,2-dichlorocyclopentane as an impurity. *trans*-2-Chlorocyclopentanol boils at 84°C. at 15 mm. and has d_{16} 1.174 and n_D^{16} 1.4832. When heated with 25 per cent aqueous alcohol, it is rapidly and quantitatively converted into *trans*-cyclopentane-1,2-diol. Similar treatment leaves the *cis*-compound unchanged.

2-Chlorocyclohexanol. As with cyclopentene, a mixture of two stereoisomeric chlorohydrins is produced by the action of hypochlorous acid on cyclohexene. *cis*-2-Chlorocyclohexanol is a liquid with b.p. 76°C. (15 mm.)[36] and n_D^{16} 1.4860. Boiling aqueous alcohol has little effect on it. *trans*-2-Chlorocyclohexanol, on the other hand, is a solid melting at 29°C. It boils at 87°C. at 15 mm. and is slowly changed by aqueous alcohol at 90°C. into *trans*-cyclohexane-1,2-diol and cyclopentylformaldehyde. The latter furnishes a semicarbazone melting at 123 to 124°C.

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[30] For a study of the tertiary system: water, butene-2 chlorohydrin and dichloride, see I. N. Bushmakin, M. M. Gol'dman and K. I. Kuchinskaya, *Sintet. Kauchuk*, 1935, 4 (1), 33; *Chem. Abs.*, 1935, **29**, 4248; *Brit. Chem. Abs.* **A**, 1936, 290. See also V. S. Batalin and P. G. Ugriumov, *loc. cit.*

[31] M. V. Likhosherstov and A. A. Petrov, *J. Gen. Chem. (U.S.S.R.)*, 1935, **5**, 1348; *Chem. Abs.*, 1936, **30**, 2174.

[32] British P. 402,880, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 2726; *Brit. Chem. Abs.* **B**, 1934, 267; *J. Inst. Pet. Tech.*, 1934, **20**, 115A.

[33] H. Nilsson and L. Smith, *Z. physik. Chem.*, 1933, **A166**, 136; *Chem. Abs.*, 1934, **28**, 465; *Brit. Chem. Abs.* **A**, 1933, 1124.

[34] A. Michael, *J. pr. Chem.*, 1899, (2) **60**, 286, 409; *J.C.S.*, 1900, **78** (1), 321; L. Henry, *Rec. trav. chim.*, 1907, **26**, 127; *Chem. Abs.*, 1907, **1**, 2079. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

[35] M. Godchot, M. Mousseron and R. Granger, *Compt. rend.*, 1935, **200**, 748; *Chem. Abs.*, 1935, **29**, 3656; *Brit. Chem. Abs.* **A**, 1935, 616.

1-Methyl-4-chlorocyclohexan-3-ol. Two stereoisomers of this composition may be isolated from the mixture of four chlorohydrins resulting from the reaction between hypochlorous acid and 1-methyl-Δ^3-cyclohexene. One of these (b.p. 79°C. at 16 mm.) is unchanged on boiling with water at 90°C. Another (b.p. 101 to 102°C. at 16 mm.) is partially converted under these conditions into *trans*-1-methylcyclohexane-3-4-diol (m.p. 63°C.) and 1-methyl-3-cyclopentylformaldehyde. The semicarbazone of this aldehyde melts at 133°C.

2-Chlorocycloheptanol. The action of hypochlorous acid on cycloheptene appears to give only one chlorohydrin. This compound, b.p. 98°C. (16 mm.), d_{19} 1.1351 and n_D 1.4948,[37] is completely transformed by boiling with aqueous alcohol into cyclohexylformaldehyde. The semicarbazone of this aldehyde melted at 167° to 168°C.

2-Chlorocyclooctanol. This substance boils at 128° to 130°C. at 20 mm. pressure. Prolonged heating with aqueous alcohol at 90°C. produces cyclooctadiene without the formation of a glycol or of the aldehyde of cycloheptane.

Bartlett and his co-workers prepared the chlorohydrins of methylcyclopentene and methylcyclohexene by two procedures. In the first, with Grignard's reagent, the *cis* isomer was formed, while the *trans* compound resulted from the action of hypochlorous acid on the cyclic monolefin.

2-Chloro-1-methylcyclopentanol.[38] The *cis* compound is obtained when 2-chlorocyclopentanone reacts with methyl magnesium bromide. It boils at 61 to 64°C. at 7 mm. and has d_{24} 1.131 and n_D^{24} 1.477. The corresponding characteristics for the *trans* isomer (from the olefin and hypochlorous acid) are b.p. 50° to 57°C. (8 mm.), d_{24} 1.059 and n_D^{24} 1.4709.

2-Chloro-1-methylcyclohexanol.[39] By the interaction of 2-chlorocyclohexanone with methyl magnesium bromide a 55 to 82 per cent yield of *cis*-2-chloro-1-methylcyclohexanol may be secured. This chlorohydrin boils at 73° to 75°C. at 15 mm. and has d_{25} 1.0995 and n_D^{25} 1.4775. It remains unchanged on distillation with quinoline, but after refluxing for one hour methylcyclohexadiene is produced. The action of 33 per cent sodium hydroxide solution (or heating with water at 200°C.), gives methylcyclopentyl ketone. *trans*-2-Chloro-1-methylcyclohexanol, from hypochlorous acid and methylcyclohexene, is a liquid of b.p. 90 to 95°C. at 28 mm., d_{26} 1.006 and n_D^{25} 1.4850. Shaking with 20 per cent cold sodium hydroxide solution gives 1-methyl-1,2-epoxycylohexane. Refluxing with 14 per cent sodium hydroxide for three hours produces *trans*-1-methylcyclohexane-1,2-diol.

When dimethylpentenol[40] is treated with hypochlorous acid, the product obtained is not the expected chlorohydrin of tetramethylglycerol, viz:

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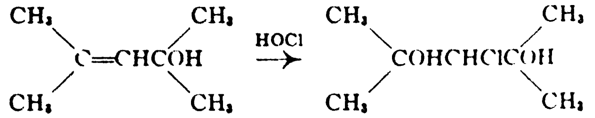
[36] See also British P. 402,880, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 2726; *Brit. Chem. Abs.* **A**, 1934, 267; *J. Inst. Pet. Tech.*, 1934, **20**, 115A, which gives boiling point as 75° to 78°C. (9 mm.).

[37] M. Godchot and Mlle. Cauquil, *Compt. rend.*, 1928, **186**, 375, 955; *Chem. Abs.*, 1928, **22**, 1335; *Brit. Chem. Abs.* **A**, 1928, 410, 634. The 2-chlorocycloheptanol is prepared also from cycloheptene by the action of $NH_2CONHCl$. Some reactions, e.g., with methyl magnesium iodide in ether solution, as well as certain physiological properties, of 2-chlorocycloheptanol are described.

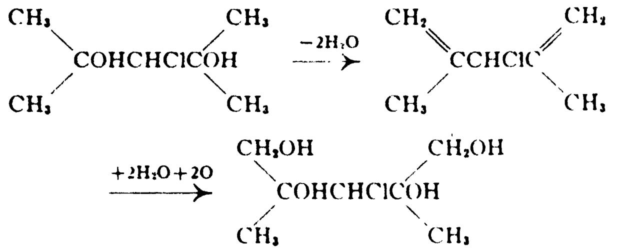
[38] P. D. Bartlett and R. V. White, *J.A.C.S.*, 1934, **56**, 2785; *Chem. Abs.*, 1935, **29**, 731; *Brit. Chem. Abs.* **A**, 1935, 208.

[39] P. D. Bartlett and R. H. Rosenwald, *J.A.C.S.*, 1934, **56**, 1990; *Chem. Abs.*, 1934, **28**, 6704; *Brit. Chem. Abs.* **A**, 1934, 1221.

[40] M. Veiller, *Compt. rend.*, 1934, **198**, 1704; *Chem. Abs.*, 1934, **28**, 5039; *Brit. Chem. Abs.* **A**, 1934, 753.



The latter compound may be formed as an intermediate, but apparently loses water and becomes oxidized at the points of unsaturation, thus:

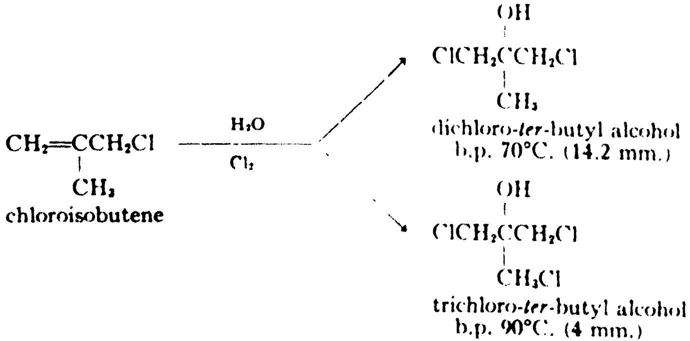


The product finally obtained, a tetrahydric alcohol, melts at 132°C.

In a process described by Cook[41] for the preparation of higher chlorohydrins which are insoluble in water, the liquid olefin, e.g., octene, is treated with an aqueous solution of hypochlorous acid, prepared from sodium bicarbonate and chlorine. The weak hypochlorous acid solution employed, containing not less than 0.75 per cent of HOCl, is intermittently regenerated while out of contact with the olefins and chlorohydrin in order to prevent the formation of dichloride.

CHLOROHYDRINS OF HALOGENATED OLEFINS

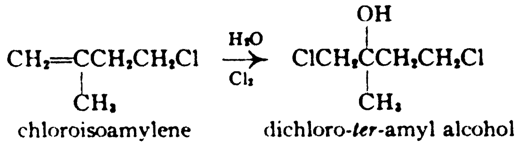
Some higher chlorohydrins of monohalogeno-alkenes have been prepared by Groll and Hearne.[42] The unsaturated monohalide, containing not less than four carbon atoms and having the halogen atom attached to saturated carbon, is treated with hypochlorous acid. An addition takes place in the usual way at the double linking, unless the latter is attached to tertiary carbon, when chlorination alone takes place. In some cases both hypochlorous acid and chlorine are added on. The reaction takes place in a similar manner when chlorine water or alkyl or aralkyl hypochlorites and water are used instead of hypochlorous acid. Some examples given by Groll and Hearne are presented below. For instance, chloroisobutene furnishes both dichloro- and trichloro-*ter*-butyl alcohol.



[41] L. W. Cook, U. S. P. 1,904,677, April 18, 1933, to Texas Co.; *Brit. Chem. Abs.* B, 1933, 998; *Chem. Abs.*, 1934, **28**, 3482.

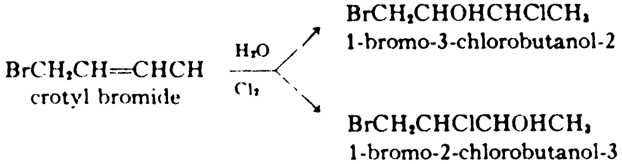
[42] H. P. A. Groll and G. Hearne, British P. 435,096, 1935, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* B, 1935, 1129; *Chem. Abs.*, 1936, **30**, 1067. French P. 789,289, 1935; *Chem. Abs.*, 1936, **30**, 1812. U. S. P. 2,062,002, Nov. 24, 1936, to Shell Development Co.; *Chem. Abs.*, 1937, **31**, 708.

Chloroisoamylene, on the other hand, yields only one product.



$$\underset{\text{chloroisoamylene}}{\underset{\displaystyle CH_3}{CH_2{=}\overset{}{C}CH_2CH_2Cl}} \xrightarrow[Cl_2]{H_2O} \underset{\text{dichloro-}\textit{ter}\text{-amyl alcohol}}{ClCH_2\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{C}}CH_2CH_2Cl}$$

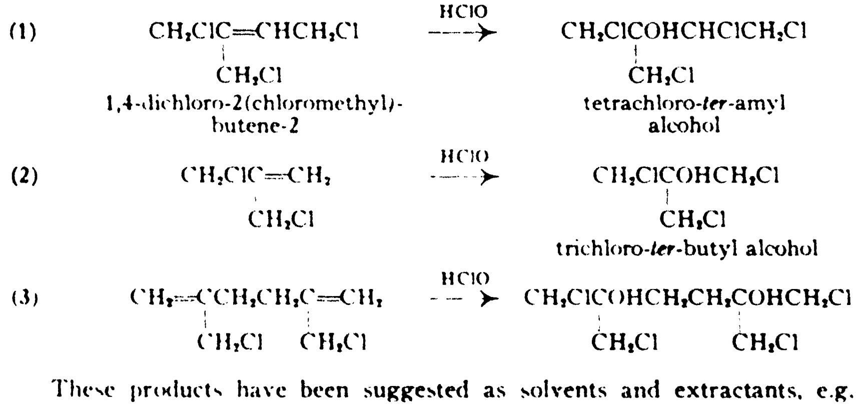
Crotyl bromide, a halogenated straight-chain olefin (as contrasted with branched-chain olefins), gives two halogenated alcohols.



$$\underset{\text{crotyl bromide}}{BrCH_2CH{=}CHCH} \xrightarrow[Cl_2]{H_2O} \begin{cases} BrCH_2CHOHCHClCH_3 & \text{1-bromo-3-chlorobutanol-2} \\ BrCH_2CHClCHOHCH_3 & \text{1-bromo-2-chlorobutanol-3} \end{cases}$$

These above-mentioned reactions take place at room temperature. The resulting polyhalogenated tertiary alcohols are intermediates for the preparation of unsaturated aldehydes and ketones, polyhydric alcohols and other derivatives which may be used for making resins or perfumes.

Polyhalogenated olefins may be substituted for the monohalogenated analogues, in which case alcohols containing three or more halogen atoms per molecule are obtained.[43] Combinations of this type can be represented in the following manner:



$$(1)\quad \underset{\text{1,4-dichloro-2(chloromethyl)-butene-2}}{CH_2Cl\underset{\displaystyle CH_2Cl}{C}{=}CHCH_2Cl} \xrightarrow{HClO} \underset{\text{tetrachloro-}\textit{ter}\text{-amyl alcohol}}{CH_2Cl\underset{\displaystyle CH_2Cl}{C}OHCHClCH_2Cl}$$

$$(2)\quad CH_2Cl\underset{\displaystyle CH_2Cl}{C}{=}CH_2 \xrightarrow{HClO} \underset{\text{trichloro-}\textit{ter}\text{-butyl alcohol}}{CH_2Cl\underset{\displaystyle CH_2Cl}{C}OHCH_2Cl}$$

$$(3)\quad CH_2{=}\underset{\displaystyle CH_2Cl}{C}CH_2CH_2\underset{\displaystyle CH_2Cl}{C}{=}CH_2 \xrightarrow{HClO} CH_2Cl\underset{\displaystyle CH_2Cl}{C}OHCH_2CH_2\underset{\displaystyle CH_2Cl}{C}OHCH_2Cl$$

These products have been suggested as solvents and extractants, e.g., in the refining of mineral oils and purification of refinery and manufactured gases. The polyhalogenated alcohols may also be hydrolyzed to polyhydric alcohols.

Groll and Hearne[44] have converted polyhydric alcohols containing a greater number of halogen atoms than hydroxyl groups into oxy-compounds having fewer chlorine atoms. The reaction may be accomplished by contact with a non-oxidizing basic metallic oxide or hydroxide or by means of basic organic compounds such as amines. For example, dichlorotertiary butyl alcohol treated with a slurry of lime produced an 80 per cent yield of methyl epichlorohydrin (1) and a lesser amount of β-methyl glycerol (2). These changes may be indicated as follows:

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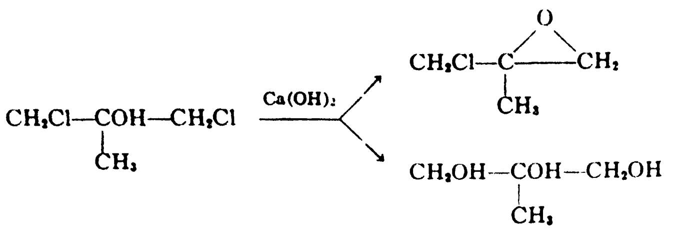
[43] H. P. A. Groll and G. Hearne, British P. 436,357, 1935, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* B, 1936, 54; *Chem. Abs.*, 1936, 30, 1812; *J. Inst. Pet. Tech.*, 1935, 21, 460A. French P. 789,290, 1935; *Chem. Abs* 1936, 30, 1812. U. S. P. 2,062,002, Nov. 24, 1936, to Shell Development Co.; *Chem. Abs.*, 1937, 31, 708.

[44] H. P. A. Groll and G. Hearne, U. S. P. 2,061,377, Nov. 17, 1936, to Shell Development Co.; *Chem. Abs.*, 1937, 31, 704.



(1)

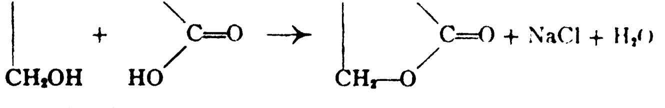
(2)

The epichlorohydrin boiled at 122°C. under atmospheric pressure. It represents a class of compounds useful as solvents for cellulose esters, as extractant agents in the separation and refining of mineral and vegetable oils, and as chemical intermediates for the production of a variety of other organic substances.

Chlorohydrins in Chemical Snytheses

Due to the presence of a reactive halogen (chlorine) atom in the molecule, 1,2-halohydrins are important intermediates in many chemical syntheses. For example, distillation of these compounds, particularly in the presence of solid alkalies, furnishes olefin oxides, and hydrolysis gives the corresponding glycols.[45] By interaction with ammonia (or amines) or with sodium alcoholates are obtained substituted amines or ethers, respectively. Possessing a hydroxyl group, chlorohydrins exhibit many of the characteristic properties of alcohols, e.g., esterification with organic acids to chlorinated esters.

Steimmig and Wittwer[46] report that carbonic acid esters are obtained in higher yields by the action of sodium bicarbonate on chlorohydrins than from glycols and phosgene or chlorocarbonic esters. They recommend that operations be carried out at atmospheric or slightly superatmospheric pressure. Thus, ethylene glycol carbonate is obtained in 80 per cent yield by heating equimolecular proportions of ethylene chlorohydrin and sodium bicarbonate for several hours. When no more sodium bicarbonate remains, the unchanged ethylene chlorohydrin and the water formed during the reaction are removed by distillation. The hot residue is then filtered from the sodium chloride, and, on cooling, a mass of crystals of ethylene glycol carbonate separates.



1,2-Propene glycol carbonate, a viscous liquid having specific gravity of about 1.21, dissolves with difficulty in water. It boils at 110°C. (at 12 mm. pressure) with partial decomposition. To prepare this compound two moles of 1,2-propene chlorohydrin are heated to boiling under reflux with one mole of sodium bicarbonate, together with a quantity of ethylene chloride or benzene. These last-named solvents form binary mixtures of low boiling point with water, which is thus continuously removed as it is formed during the reaction. Operations are stopped when all the alkali has disappeared. The chlorohydrin is distilled off and the hot residue filtered. From the resulting mixture of 1,2-propene glycol and

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[45] For a review of the reactions of chlorohydrins, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. See also Chapters 22 and 23.

[46] G. Steimmig and M. Wittwer, U. S. P. 1,907,891, May 9, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3721.

1,2-propene glycol carbonate, the latter (about 30 per cent of the mixture) is obtained in a pure state by fractional distillation followed by freezing of the distillate.

When an aqueous solution of ethylene chlorohydrin is treated with an alkali metal resorcinolate at 50-55°C. for 24 hours under a reflux, resorcinol β-hydroxyethyl ether is obtained.[47] This material is a solid, melting at 83.1-83.4°C., boiling at 214°C. (20 mm.), and soluble in water, ether and benzene. Motwani and Wheeler[48] point out that either the mono- or di-β-hydroxyethyl ether may be obtained by regulating the proportions of reactants. These ethers furnish the corresponding mono- or di-β-chloro derivatives, respectively, on treatment with phosphorus pentachloride.

On heating the halohydrin with thionyl chloride, β-chloroethyl sulphite is formed.[49] Komissarov[50] studied this reaction and found that on using a slight

$$2ClCH_2CH_2OH + SOCl_2 \longrightarrow (ClCH_2CH_2O)_2SO + 2HCl$$

excess (5 per cent) of thionyl chloride in the cold, β-chloroethyl chlorosulphinate is first produced.

$$ClCH_2CH_2OH + SOCl_2 \longrightarrow ClCH_2CH_2OSOCl + HCl$$

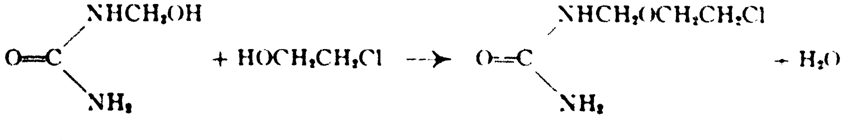
If more of the halohydrin is then added and the mixture heated for 3 hours at 50° to 60°C., β-chloroethyl sulphite is obtained.

$$ClCH_2CH_2OSOCl + ClCH_2CH_2OH \longrightarrow HCl + (ClCH_2CH_2O)_2SO$$

The latter may be reconverted into the chlorosulphinate (at room temperature) by the action of thionyl chloride.

β-Chloroethyl sulphite boils at 147-150°C. at 10 mm., and at 117.5-118°C. at 4 mm. It has d_4^{20} 1.4255, d_0^0 1.444, and n_D^0 1.481. β-Chloroethyl chlorosulphinate boils at 93° to 95°C. at 40 mm. and at 84 to 85°C. at 20 mm. and has d_4^{20} 1.5010.

Condensations with Ureas. Synthetic resins and condensation products resembling linoxyn and waxes, which can be employed in the manufacture of lacquers and plastics, are made by condensing urea or methylol urea with ethylene chlorohydrin.[51] Reaction with monomethylol urea is carried out at 90°C. in the presence of a small proportion of urea nitrate. It proceeds according to the equation:



$$O{=}C\begin{matrix}\diagup NHCH_2OH\\ \diagdown NH_2\end{matrix} + HOCH_2CH_2Cl \longrightarrow O{=}C\begin{matrix}\diagup NHCH_2OCH_2CH_2Cl\\ \diagdown NH_2\end{matrix} + H_2O$$

The product may then be combined (a) with sodium acetate to form an ester; (b) with sodium methoxide to give an ether; or (c) with the sodium salt of the acid methyl ester of oxalic acid to give a di-ester.

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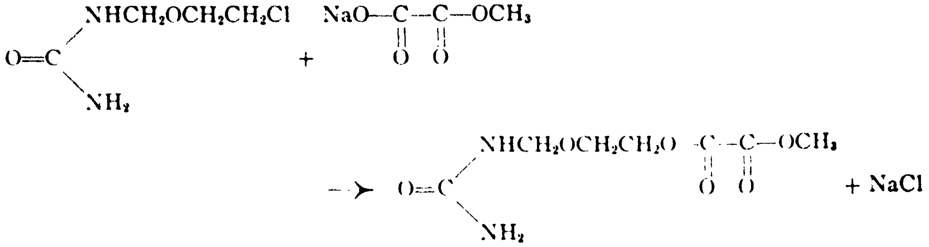
[47] L. P. Kyrides, U. S. P. 2,015,115, Sept. 24, 1935, to National Aniline and Chemical Co.; *Chem. Abs.*, 1935, **29**, 7346; *Brit. Chem. Abs.* **B**, 1936, 1083.

[48] D. C. Motwani and T. S. Wheeler, *J. Univ. Bombay*, 1935, **4**, 104; *Chem. Abs.*, 1936, **30**, 5197; *Brit. Chem. Abs.* **A**, 1936, 839.

[49] R. Levaillant, *Compt. rend.*, 1929, **189**, 465; *Chem. Abs.*, 1930, **24**, 824; *Brit. Chem. Abs.* **A**, 1929, 1269.

[50] J. F. Komissarov, *J. Gen. Chem. (U.S.S.R.)*, 1933, **3**, 309; *Chem. Abs.*, 1934, **28**, 2324; *Brit. Chem. Abs.* **A**, 1933, 1274.

[51] W. Punga, K. Eisenmann, E. Scholz and T. Kollmann, U. S. P. 1,963,762, June 19, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5263. German P. 540,071, 1929; *Chem. Abs.*, **1932**, **26**, **1812**.



Reaction of the monomethylol urea-ethylene chlorohydrin condensation product with sodium linoleate at 120°C. for 12 hours gave a yellow-brown resin resembling linoxyn and suggested as a binding agent in laminated and molded articles.

Reactions with Mercaptans. Ethylene chlorohydrin may also be employed in the preparation of certain aliphatic sulphides of high molecular weight, as, for example, the product from α-dodecylthiol and the halohydrin. These have a soapy character and may be used in the production of detergents, emulsifying agents and various textile assistants, as well as in the rubber and pharmaceutical industries.[52]

Windus and Shildneck[53] report that methyl mercaptan (dissolved in alkaline medium) combines with ethylene chlorohydrin to furnish β-hydroxyethyl methyl sulphide. In this instance, the mercaptan was made by decomposition of dimethyl isothiourea sulphate[54] with aqueous sodium hydroxide.

$$HN{=}C(SCH_3)NH_2]_2 \cdot H_2SO_4 + 2NaOH \longrightarrow HN{=}CNH_2 \cdot NHCN + 2CH_3SH + Na_2SO_4 + 2H_2O$$

The hydroxy thioether may be converted into the corresponding β-chloroethyl methyl sulphide by the action of thionyl chloride.[55]

$$CH_3SCH_2CH_2OH + SOCl_2 \longrightarrow CH_3SCH_2CH_2Cl + SO_2 + 2HCl$$

Sulphur-containing compounds are said to be obtained by the interaction of acetals of ethylene chlorohydrin and ammonium, alkali or alkaline-earth sulphides or polysulphides.[56] Combination of the reactants may proceed in the presence of water.

Arsenic Derivatives. Soare[57] has described the preparation of β-haloethylarsines from ethylene chlorohydrin. He gives the following details for making β-bromoethyl arsenic dibromide: 100 g. of ethylene chlorohydrin were added with constant stirring to a solution of sodium arsenite obtained by adding 100 g. of arsenious oxide to 120 g. of sodium hydroxide in 300 cc. of water. The temperature of the mixture was maintained at 5 to 10°C. and the progress of the reaction followed by taking a test portion from time to time, acidifying with hydrochloric acid, neutralizing with sodium bicarbonate and titrating the arsenious oxide with 0.1*N* iodine. After 3 to 4 hours it was found that 80 to 85 per cent of the arsenic had combined. Stirring was then stopped and the sodium chloride formed removed by filtration. The filtrate was neutralized (using Congo red as an indicator), concentrated in vacuo at a low temperature, filtered, and extracted with absolute alcohol. The residue, consisting of impure β-hydroxyethanearsonic acid, $HOC_2H_4AsO(OH)_2$, was next converted into β-hydroxyethylarsenous oxide, HOC_2H_4AsO, by heating an aqueous solution on the water bath at 60°C. for 2 hours in an atmosphere of sulphur dioxide. Treatment in the cold with potassium bromide and sulphuric acid produced a brown liquid which was extracted with chloroform. From the residue, β-bromoethylarsenic dibromide was finally obtained by distillation under reduced pressure. This dibromide is a colorless crystalline solid (m.p. 36°C., b.p. 110°C. at 25 mm.) which slowly decomposes unless kept perfectly dry. On treatment with warm aqueous sodium hydroxide, it yielded ethylene quantitatively.[58]

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[52] British P. 412,305, 1933, to Henkel & Co. G.m.b.H.; *Brit. Chem. Abs.* **B**, 1934, 751; *Chem. Abs.*, 1934, **28**, 7594. French P. 748,460, 1933; *Chem. Abs.*, 1933, **27**, 5340.

[53] W. Windus and P. P. Shildneck, "Organic Syntheses," John Wiley & Sons, Inc., New York, 1934, **14**, 54; *Chem. Abs.*, 1934, **28**, 2671.

[54] For the preparation of this compound, see P. P. Shildneck and W. Windus, "Organic Syntheses," John Wiley & Sons, Inc., New York, 1932, **12**, 52; *Chem. Abs.*, 1932, **26**, 1484.

[55] W. R. Kirner and W. Windus, "Organic Syntheses," John Wiley & Sons, Inc., New York, 1934, **14**, 18; *Chem. Abs.*, 1934, **28**, 2671.

[56] British P. 450,218, 1936, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech.*, 1936, **22**, 464A.

[57] A. G. Soare, *Bul. chim. soc. române chim.*, 1933, **36**, 75; *Chem. Abs.*, 1935, **29**, 2506; *Brit. Chem. Abs.* **A**, 1934, 1341.

Reaction with Amines. β-Diethylaminoethyl alcohol is prepared by heating diethylamine and ethylene chlorohydrin[59] in the presence of sodium hydroxide in an autoclave for 3 hours at 160°C.:

$$(C_2H_5)_2NH + ClCH_2CH_2OH + NaOH \longrightarrow (C_2H_5)_2NCH_2CH_2OH + NaCl + H_2O$$

Hartman[60] reports a yield of 68 to 70 per cent of the theoretical amount by this method. According to Headlee, Collett and Lazzel,[61] this amino-alcohol is a liquid with the following physical properties: b.p. 160°C. (741 mm.), 100°C. (80 mm.), 96°C. (73 mm.) and 55°C. (10 mm.); n_D^{25} 1.4389, d_{abs}^{25} 0.0405, and surface tension of 27.50 dynes per cm. at 26.5°C.

In a process developed by Lehmann[62] equimolecular proportions of the amine and halohydrin are allowed to react in a liquid medium (e.g., methyl alcohol) containing an alkali. Mono-N-alkanol derivatives of the aromatic diamines or polyamines are formed. These are described as being basic in character, readily soluble in water or alcohol, difficultly so in ether, and insoluble in aliphatic hydrocarbons. They furnish salts which may be dissolved in water. The alkanol amines are suggested as intermediates in the preparation of dyes.

Another field for the use of ethylene chlorohydrin is in the preparation of compositions for waterproofing fabrics. One component of such mixtures may be nonwetting protective colloids[63] resulting from the condensation of ethylene chlorohydrin (or ethylene oxide) with various insoluble organic compounds containing a hydroxyl or amino group and at least six carbon atoms. Acrylic acid esters, their homologues and polymers may be employed in the production of resins for use in the manufacture of laminated safety glass, lacquers, varnishes and electrical insulating media.[64] A synthesis of these esters, developed by Bauer,[65] is based on the use of ethylene chlorohydrin as a starting material. This is reacted with sodium cyanide to furnish the nitrile. The latter, in turn, is converted into an ester of acrylic acid by treatment with an alcohol in the presence of an acid. The reaction involved may be summarized in the two equations:

$$CH_2OHCH_2Cl + NaCN \longrightarrow CH_2OHCH_2CN + NaCl$$
$$CH_2OHCH_2CN + ROH + H_2SO_4 \longrightarrow CH_2{=}CHCOOR + NH_4HSO_4$$

[58] V. V. Nekrasov and A. S. Nekrasov, *Ber.*, 1928, **61**, 1816; *Chem. Abs.*, 1929, **23**, 91; *Brit. Chem. Abs.* **A**, 1928, 1230.

[59] A. Ladenburg, *Ber.*, 1881, **14**, 1878. Also M. A. Sodermann and T. B. Johnson, *J.A.C.S.*, 1925, **47**, 1394; *Chem. Abs.*, 1925, **19**, 1700; *J.S.C.I.*, 1925, **44**, 567B.

[60] W. W. Hartman, "Organic Syntheses," John Wiley & Sons, Inc., New York, 1934, **14**, 28; *Chem. Abs.*, 1934, **28**, 2678.

[61] A. J. W. Headlee, A. R. Collett and C. L. Lazzell, *J.A.C.S.*, 1933, **55**, 1066; *Chem. Abs.*, 1933, **27**, 1861; *Brit. Chem. Abs.* **A**, 1933, 493.

[62] F. Lehmann, U. S. P. 2,022,245, Nov. 26, 1935, to General Aniline Works; *Chem. Abs.*, 1936, **30**, 1391.

[63] British P. 401,712, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1934, 142; *Chem. Abs.*, 1934, **28**, 2861.

[64] H. T. Neher, *Ind. Eng. Chem.*, 1936, **28**, 267; *Chem. Abs.*, 1936, **30**, 8429.

[65] W. Bauer, U. S. P. 1,388,018, Aug. 16, 1921, to Röhm & Haas A.-G.; *Chem. Abs.*, 1921, **15**, 4011; *J.S.C.I.*, 1921, **40**, 790A. U. S. P. 1,829,208, Oct. 27, 1931; *Chem. Abs.*, 1932, **26**, 735.

β,β'-DICHLORODIETHYL ETHER

This compound, $ClCH_2CH_2OCH_2CH_2Cl$, is formed when ethylene chlorohydrin is treated simultaneously with chlorine and an excess of ethylene at 80°C.[66] At the end of the reaction, water is added and the mixture distilled. An 85 per cent yield of the ether is reported, ethylene dichloride being formed as a by-product. The ether is a liquid of boiling point 178°C., freezing point $-$ 51.7°C., and $d\,^{20}_{20}$ 1.222. Its toxicity has been investigated by Schrenk, Patty and Yant,[67] who concluded that the odor and the irritant properties of this substance give ample warning of its presence in concentrations likely to prove dangerous.

In various ways this chloro-ether has assumed commercial importance. It reacts with metallic polysulphides (e.g., Na_2S_4) to give products resembling rubber.[68] Condensed with substituted phenols or naphthols in the presence of sodium hydroxide it furnishes plasticizers which may be incorporated in cellulose ester lacquers and analogous compositions.[69] Other industrial applications are as a liquid medium for the hydrolysis of cellulose acetate,[70] as an ingredient in cellulose acetate dopes and lacquers,[71] and in the preparation of morpholine derivatives.[72] N-substituted morpholines are prepared by the action of β,β'-dichlorodiethyl ether on a primary amine, such as aniline, in the presence of an inorganic base. These are suggested as dye intermediates, rubber antioxidants, acid and corrosion inhibitors.

By the action of fused potassium hydroxide on β,β'-dichlorodiethyl ether in an atmosphere of ammonia, Major and Ruigh[73] produce practically pure divinyl ether, $CH_2{=}CHOCH{=}CH_2$. Lott[74] accomplishes the same conversion by adding the dichloroether under pressure to a solution of potassium hydroxide in diethylene glycol at 210-240°C. Divinyl ether is a liquid boiling[74a] at 28.3°C. at 760 mm. Much interest has been shown in the use of this ether in anesthesia.[74b] The compound is said to be more toxic than diethyl ether but less so than chloroform.[74c] Since with divinyl ether, anesthesia is rapidly induced, easily maintained and subsequent recovery is rapid, the substance is considered widely useful in operative procedures of short duration.[75] The ether containing a small percentage of a non-volatile stabilizer (about 0.01 per cent) and about 3.5 per cent ethanol as an anti-freeze is known as vinethene.[75a] Suggested stabilizers include polyphenols, e.g., hydroquinone, and aromatic amines, e.g., N.N′-diphenyl phenylene diamine and phenyl-α-naphthylamine.[75b]

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[66] G. A. Perkins, British P. 438,271, 1934; *Chem. Abs.*, 1936, **30**, 2578, *Brit Chem. Abs.* **B**, 1936, 138. French P. 773,140, 1934; *Chem. Abs.*, 1935, **29**, 1432. Both patents to Carbide and Carbon Chemicals Corp.

[67] H. H. Schrenk, F. A. Patty and W. P. Yant, *U. S. Pub. Health Repts.*, 1933, **48**, 1389; *Chem. Abs.*, 1934, **28**, 528.

[68] J. C. Patrick, *Trans. Far. Soc.*, 1936, **32**, 347; *Chem. Abs.*, 1936, **30**, 2462. See also British P. 439,355, May 31, 1934; *Brit. Chem. Abs.* **B**, 1936, 206.

[69] British P. 403,667, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 3584; *Brit. Chem. Abs.* **B**, 1934, 210.

[70] C. S. Webber and C. J. Staud, U. S. P. 1,905,536 and 1,905,537, April 25, 1933, to Eastman Kodak Co.; *Brit. Chem. Abs.* **B**, 1934, 13; *Chem. Abs.*, 1933, **27**, 3605. The chloroethyl ether, in the presence of acetic acid, is said to constitute a solvent for both types of cellulose acetate and also for the hydrolyzing agents.

[71] E. W. Reid, Canadian P. 347,857, 1935, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, **29**, 3074.

[72] British P. 438,452, 1935, to E. I. du Pont de Nemours & Co; *Chem. Abs.*, 1936, **30**, 2579.

[73] R. T. Major and W. L. Ruigh, U. S. P. 2,021,872, Nov. 19, 1935, to Merck & Co.; *Chem. Abs.*, 1936, **30**, 492.

[74] W. A. Lott, U. S. P. 2,013,662, Sept. 10, 1935, to E. R. Squibb & Sons; *Brit. Chem. Abs.* **B**, 1936, 972; *Chem. Abs.*, 1935, **29**, 6908.

[74a] W. A. Lott and W. G. Christiansen, *Pub. Chem. Pharm. Research Labs., E. R. Squibb & Sons*, June, 1934; *Chem. Abs.*, 1934, **28**, 5401.

[74b] S. Goldschmidt, I. S. Ravdin, B. Lucke, G. P. Muller, C. G. Johnston and W. L. Ruigh, *J. Am. Med. Assoc.*, 1934, **102**, 21; *Chem. Abs.*, 1935, **29**, 2229. S Goldschmidt, I. S. Ravdin and B. Lucke, *Am. J. Med. Sci.*, 1933, **186**, 888; *Chem. Abs.*, 1934, **28**, 2416. W. Bourne and D. W. Sparling, *Anesthesia and Analgesia*, 1935, **14**, 1; *Chem. Abs.*, 1935, **29**, 3401. W. Bourne, *J. Am. Med. Assoc.*, 1935, **105**, 2047; *Can. Med. Assoc. J.*, 1935, **33**, 629; *Chem. Abs.*, 1936, **30**, 771. W. Bourne and B. B. Raginsky, *Brit. J. Anesthesia*, 1935, **12** (2), 62; *Chem. Abs.*, 1936, **30**, 771. F. W. Marvin, *Anesthesia and Analgesia*, 1935, **14**, 257; *Chem. Abs.*, 1936, **30**, 766. F. F. Shipway, *Lancet*, **1935** (1), 82; *Chem. Abs.*, 1935, **29**, 2306. J. Connolly and R. F. Baker, *U. S. Naval Med. Bull.*, 1936, **34**, 499; *Chem. Abs.*, 1936, **30**, 8376. *Cf.* also Chapter 53 on the use of petroleum hydrocarbons in anesthesia.

[74c] See H. Molitor, *J. Pharmacol.*, 1936, **57**, 274; *Chem. Abs.*, 1936, **30**, 7222.

β-Chloroethyl-β′-chloroisopropyl ether, $ClCH_2CH_2OCH(CH_3)CH_2Cl$, a liquid boiling at 65°C. (8 mm.), is prepared from ethylene chlorohydrin, chlorine and propene.[75c] Other bis-β-dichlorodialkyl ethers[76] may be synthesized by employing the appropriate olefin and alkene chlorohydrin. According to Cox,[77] the reaction, in the presence of water, between ethylene chlorohydrin, chlorine and ethylene, at temperatures between 20°C. and 100°C., leads to the formation of β-chloroethyl-β-chloroethoxyethyl ether, $ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$. This water-insoluble liquid, suggested for high-pressure lubrication, boils at 230°C. at 760 mm., and at 118°C. at 10 mm.

Interaction of β,β′-dichlorodiethyl ether with a Grignard reagent,[78] such as magnesium-phenylbromide, in xylene, at 140°C., results in the formation of di-β-phenylethyl ether, b.p. 162-165°C. (7 mm.). By analogous reactions such compounds as the following may be prepared: γ,γ′-diphenyldipropyl ether, b.p. 200-210°C. (5 mm.) and β-chloro-β′-phenyldiethyl ether, b.p. 100-110°C. (2 mm.). Subsequent treatment of the diethyl ethers yields substituted alcohols or alcoholic derivatives.

THE CHLOREX PROCESS

The use of β,β′-dichlorodiethyl ether in the refining of lubricating oils has been referred to previously. The value of this solvent is enhanced by its physical properties, the high specific gravity making for rapid separation of the two phases formed with oils, and its relatively low boiling point rendering recovery a comparatively simple matter. Furthermore, extraction temperatures are not high (10° to 52°C.), so that plant costs and evaporation losses are both low. The main effect of Chlorex treatment is to improve the viscosity index[79] of the lubricant, which may be increased even when the original figure is high as in the case of Pennsylvania residua. Also, some treated distillates are reported to exhibit a high resistance to sludging and oxidation.[80]

[75] I. S. Ravdin, E. L. Eliason, G. M. Coates, T. B. Holloway, L. K. Ferguson, A. B. Gill and T. J. Cook, *J. Am. Med. Assoc.*, 1937, **108**, 1163.

[75a] L. Rosenthaler, *Schweiz. Apoth.-Ztg.*, 1935, **73**, 633; *Chem. Abs.*, 1936, **30**, 3401.

[75b] R. T. Major and W. L. Ruigh, U. S. P. 2,044,800 and 2,044,801, June 23, 1936, to Merck & Co.; *Chem. Abs.*, 1936, **30**, 5728. K. Merck, L. Merck, W. Merck and F. Merck (Firm of E. Merck), British P. 445,289, 1936; *Chem. Abs.*, 1936, **30**, 6513.

[75c] C. A. Perkins, *loc. cit.*

[76] The corresponding β,β′-dichloromethyl ether may be produced by chlorination of dimethyl ether. The reaction is carried out in the presence of an inert solvent and may be catalyzed by metals, metallic chlorides and actinic light. See P. L. Salzberg and J. H. Werntz, U. S. P. 2,065,400, Dec. 22, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, **31**, 1046.

[77] H. L. Cox, U. S. P. 2,017,811, Oct. 15, 1935, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, **29**, 8320; *Brit. Chem. Abs.* **B**, 1936, 1141.

[78] H. B. Gans, Jr. and A. B. Holton, U. S. P. 2,013,752, Sept. 10, 1935; *Brit. Chem. Abs.* **B**, 1936, 1083; *Chem. Abs.* 1935, **29**, 6902.

[79] Chapter 50 of this volume discusses the viscosities of petroleum oils and methods of determining viscosity indices. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

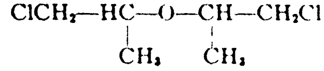
[80] For detailed descriptions of the use of Chlorex in the extraction of oils and the results of laboratory tests and plant operations, see W. H. Bahlke, A. B. Brown and F. F. Diwoky, *Refiner*, 1933, **12**, 445; *Oil and Gas J.*, 1933, **32** (23), 60; *J. Inst. Pet. Tech.*, 1934, **20**, 34A. D. B. Williams, *Oil and Gas J.*, 1934, **33** (18), 13, 16; *Chem. Abs.*, 1934, **28**, 7508; *J. Inst. Pet. Tech.*, 1935, **21**, 21A. I. R. Roseanu, *Mon. Petr. Roum.*, 1935, **36**, 1259; *J. Inst. Pet. Tech.*, 1935, **21**, 415A. H. T. Bennett, U. S. P. 2,044,603, June 16, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 407A; *Chem. Abs.*, 1936, **30**, 7841. See also, *Refiner*, 1935, **14**, 558; *J. Inst. Pet. Tech.*, 1936, **22**, 57A. Also, U. B. Bray, U. S. P. 2,031,205, Feb. 18, 1936, to Union Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 2363; *J. Inst. Pet. Tech.*, 1936, **22**, 216A. J. Robinson, U. S. P. 2,057,113, Oct. 13, 1936, to Standard Oil Co. of Indiana; *Chem. Abs.*, 1936, **30**, 8594; *J. Inst. Pet. Tech.*, 1937, **23**, 31A.

Bennett[81] separates the naphthenes from the paraffins of a lubricating oil by a single extraction with, for example, 6 parts of β,β'-dichlorodiethyl ether. Page[82] recommends diluting the oil with a light hydrocarbon such as propane, butane or propene before extraction. Other diluents which may be employed are benzene or trichloroethylene.[83] In some instances, the distillate may be subjected successively to different extracting agents, e.g., liquid sulphur dioxide followed by Chlorex.[84] Another modification comprises distilling the treated oil between each extracting operation. Liberthson[85] points out that agitating the halogenated ether with oils containing dispersed "green" acids and dissolved "mahogany" acids[86] (resulting from fuming sulphuric acid refining under sulphonating conditions) effects coagulation and precipitation of the former. Mahogany acids remain in solution in the ether layer which forms when the oil-ether mixture is allowed to settle. In this way separation of the two types of sulphonated materials may be accomplished. Page[87] suggests dichloroethyl ether as a liquid medium for the removal of oil from paraffin wax. The same chloro-ether is incorporated by Tijmstra and McKittrick[88] in a composite selective solvent for dewaxing petroleum oils.

Other chlorinated ethers, such as β,β'-dichlorodipropyl ether and β-β'-dichlorodiisopropyl ether, either alone or in admixture with propane, butane, propene or acetone, are also efficacious in the removal by selective extraction of naphthenic and other undesirable constituents of mineral or lubricating oils.[89]

Bis(β-chloroisopropyl) Ether

The preparation and properties of this compound have been described by Wickert.[90] Propene chlorohydrin (500 g.) is treated with concentrated sulphuric acid (100 g. of d 1.84) in a 5-liter flask under reflux regulated to allow removal of the water formed in the reaction. After heating to boiling for 3 hours, an equal volume of water is added to the contents of the flask. Distillation without rectification is then carried on until the distillate is free from oily particles. The ether settles as an oily layer; after separation it is dried over potassium carbonate and distilled under reduced pressure. The final product, β,β'-dichlorodiisopropyl ether, may be indicated by formula in the following manner:



$$\mathrm{ClCH_2{-}\underset{\displaystyle CH_3}{\underset{|}{HC}}{-}O{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2Cl}$$

It is a water white liquid, boiling at 187.1°C. Its density, d_{20}, is 1.1127.

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[81] H. T. Bennett, Canadian P. 342,473, 1934, to The Mid-Continent Petroleum Corp.; *Chem. Abs.*, 1934, **28**, 5976. See also H. T. Bennett, U. S. P. 2,003,2339, May 28, 1935, *Brit. Chem. Abs.* **B**, 1936, 487; *J. Inst. Pet. Tech.*, 1935, **21**, 268A.

[82] J. M. Page, Jr., Canadian P. 344,609, 1934, to The Standard Oil Co. of Ind; *Chem. Abs.*, 1935, **29**, 2346.

[83] French P. 773,764, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1935, **29**, 1617. See also A. Schaafsma and J. M. Versteeg, Canadian P. 359,459, July 28, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 6937. C. M. Kellogg, U. S. P. 2,047,826, July 14, 1936; *Chem. Abs.*, 1936, **30**, 6185.

[84] D. R. Merrill and P. Subkow, U. S. P. 1,948,042, Feb. 20, 1934, to Union Oil Co. of California; *Chem. Abs.*, 1934, **28**, 2892; *J. Inst. Pet. Tech.*, 1934, **20**, 334A. R. E. Haylett, U. S. P. 1,988,793, Jan. 22, 1935, to Union Oil Co. of California; *Chem. Abs.*, 1935, **29**, 1622; *Brit. Chem. Abs.* **B**, 1936, 87; *J. Inst. Pet. Tech.*, 1935, **21**, 139A. D. R. Merrill, U. S. P. 1,988,803, Jan. 22, 1935, to Union Oil Co. of Calif.; *Chem. Abs.*, 1935, **29**, 1919; *Brit. Chem. Abs.* **B**, 1936, 87. Also U. S. P. 2,043,389, Sept. 6, 1936; *Chem. Abs.*, 1936, **30**, 7835; *J. Inst. Pet. Tech.*, 1936, **22**, 407A.

[85] L. Liberthson, U. S. P. 2,050,345, Aug. 8, 1936, to L. Sonneborn Sons, Inc.; *J. Inst. Pet. Tech.*, 1936, **22**, 457A; *Chem. Abs.*, 1936, **30**, 6932.

[86] For a discussion of "green" acids and "mahogany" acids, see Chapter 46. Also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[87] J. M. Page, Jr., U. S. P. 2,048,513, July 21, 1936, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1936, **30**, 6185; *J. Inst. Pet. Tech.*, 1936, **22**, 458A.

[88] S. Tijmstra and D. S. McKittrick, Canadian P. 360,666, 1936; *Chem. Abs.*, 1936, **30**, 7840.

[89] S. H. Diggs and J. W. Page, Jr., U. S. P. 1,976,544, Oct. 9, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1934, **28**, 7518; *Brit. Chem. Abs.* **B**, 1935, 838. British P. 410,175, 1934; *Chem. Abs.*, 1934, **28**, 6296; *Brit. Chem. Abs.* **B**, 1934, 791; *J. Inst. Pet. Tech.*, 1934, **20**, 460A.

[90] J. N. Wickert, Canadian P. 359,236, 1936, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1936, **30**, 6011: U. S. P. 2,052,264, Aug. 25, 1936; *Chem. Abs.*, 1936, **30**, 7127.

BROMOHYDRINS DERIVED FROM OLEFINS

A few bromohydrins have been described, notably those obtained from cyclohexene and its derivatives. A general method for the synthesis of bromohydrins by the use of esters of hypobromous acid has been referred to previously.[91]

2-Bromocyclohexanol. Preparation of this compound was carried out by Hunter and Marriott[92] in the following manner. A solution of hypobromous acid was first made by gradually mixing equimolecular quantities of mercuric oxide and bromine in ice-cold water. This solution, after being rapidly filtered, was added (in slight excess) to cyclohexene. With constant agitation and cooling, the product was distilled with steam, dried and then fractionated in vacuo. 2-Bromocyclohexanol was obtained as a heavy, colorless liquid of boiling point 103° to 104°C. at 18 mm.[93] It is said to turn black very rapidly, even in the dark. A certain proportion of this compound is also formed in the preparation of *1-methyl-2-bromocyclohexan-1-ol.*[94]

Cyclohexene may be treated with the mixture of hypobromous acid and methyl hypobromite. The latter is obtained by shaking a 5 per cent methyl alcohol solution of bromine with a solution of silver nitrate in ethyl alcohol. A 50 to 60 per cent yield of 1-methyl-2-bromocyclohexan-1-ol, b.p. 76° to 77°C. (10 mm.), n_D^{20} 1.4884, d_4^{20} 1.3314, is secured. At the same time some 2-bromocyclohexan-1-ol is formed.[95] The product is obtained purer, but in smaller yield, if a methyl hypobromite reagent is used. This material is prepared by shaking a 5 per cent solution of bromine in methyl alcohol with an excess of finely divided solid silver nitrate. The nitric acid set free should be almost neutralized with calcium carbonate and the excess silver nitrate nullified by the addition of potassium acetate. It was not possible to replace the silver nitrate by sodium, barium or calcium carbonate, nor by oxide of mercury.

Methyl hypobromite alone was used in the preparation of all the following compounds:

(β-Methoxy-γ-bromopropyl) benzene (from allyl benzene and methyl hypobromite) which is a liquid of d_4^{20} 1.3191, n_D^{20} 1.5365.

(α-Metoxy-β-bromopropyl) benzene, b.p. 87° to 88°C. (0.4 mm.), n_4^{20} 1.3090, n_D^{20} 1.5338, is formed in 50 per cent yield from propenylbenzene.

α-Methoxy-β-bromodihydroanethole, obtained from anethole in 70 per cent yield, has b.p. 115° to 116°C. (0.15 mm.), d_4^{20} 1.3181 and n_D^{20} 1.5391.

Bromomethoxycyclohexene as made from cyclohexa-1,3-diene was an impure material boiling at 66° to 72°C. under 0.2 mm. pressure. A similar yield (45 to 50 per cent) of the same oily product was obtained with bromoacetamide as reagent instead of methyl hypobromite.

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[91] British P 402,880, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 2726; *Brit. Chem. Abs.* **B**, 1934, 267; *J. Inst. Pet. Tech.*, 1934, **20**, 115A

[92] L. Hunter and J. A. Marriott, *J. C.S.*, **1936**, 285; *Chem. Abs.*, 1936, **30**, 2929; *Brit. Chem. Abs.* **A**, 1936, 460.

[93] British P 402,880, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 2726; *Brit. Chem. Abs.* **B**, 1934, 267; *J. Inst. Pet. Tech.*, 1934, **20**, 115A, gives boiling point of this compound as 91 to 93°C. at 11 mm

[94] The preparation of the compound from 2-bromocyclohexanone and Grignard reagent (methyl magnesium bromide) is described by P. D. Bartlett and R. H. Rosenwald, *J. A. C. S.*, 1934, **56**, 1992; *Chem. Abs.*, 1934, **28**, 6704; *Brit. Chem. Abs.* **A**, 1934, 1221. The properties are given as boiling point 83°C. (7 mm.), d_{25} 1.360 and n_D^{25} 1.5032

[95] K. Meinel, *Ann.*, 1935, **516**, 231; *Chem. Abs.*, 1935, **29**, 3657; *Brit. Chem. Abs.* **A**, 1935, 603

Chapter 22

Production, Properties and Uses of Simple Glycols

The glycols, or dihydric alcohols, may be of two kinds, (a) those derived by the hydroxylation of olefins and which are designated α- or 1,2-glycols because the hydroxyl groups are attached to adjacent carbon atoms, and (b) those in which the hydroxyl groups are mutually more remote, as in trimethylene glycol. The large supplies of ethylene in gases from cracking operations have been found to be a raw material for the synthesis of ethylene glycol, and have thereby caused great interest in this compound.[1] Methods for the formation of glycols, of which 1,2-dihydroxyethane or ethylene glycol is the most common, depend either upon mild oxidation of the unsaturated hydrocarbon at its double bond, or hydrolysis of derivatives of alcohol.

Direct hydroxylation of an alkene may be accomplished by the use of such agents as potassium permanganate, Caro's acid (H_2SO_5) and persulphuric acid or by employment of osmium tetroxide to catalyze a mild oxidation by potassium chlorate. However, hydrolysis of derivatives of the glycols is more frequently employed.

PRODUCTION OF ETHYLENE GLYCOL

Among the substances from which glycols may be prepared are the dihaloethanes, ethylene halohydrins and glycol esters. Heating a dihaloethane and aqueous sodium carbonate in an autoclave at pressures up to 100 atmospheres is one mode of procedure. Thus, Klebanskii and Dolgopol'skii[2] found that an 82 per cent yield of glycol may be obtained by saponifying 200 g. of ethylene dichloride with 220 g. sodium carbonate for 4 hours at 150°C. and 52 atmospheres pressure. By using sodium acid carbonate ($NaHCO_3$) and heating for 36 hours at 150°C. under 58 atmospheres pressure a 92.5 per cent conversion was secured. No improvement was observed when emulsifiers such as petroleum sulphonic acids, sodium oleate or sodium stearate were added to the reaction mixture. Under semi-commercial conditions, yields of 85 to 90 per cent were procured by employing temperatures of 175° and 195°C. and 100 atmospheres pressure. Some vinyl chloride, which was separated by absorption in xylene, was also found. Weihe[3] has suggested effecting reaction between ethylene chloro- or bromo-hydrin or ethylene di-bromide or -chloride by treating with sodium hydroxide and simultaneously adding carbon dioxide.

Aqueous potassium carbonate has been used for hydrolysis of ethylene dibromide.[4] In this instance a mixture of glycol (in largest proportion) and vinyl bromide is formed, the latter by elimination of hydrogen bromide from the dibromo hydrocarbon. In the presence of a solution of potassium carbonate in equal parts of ethanol and water, the vinyl halide was the major product. On the other hand a solution of sodium hydroxide in absolute alcohol gave vinyl bromide as the only product. The latter reaction is said to be purely bimolecular, and proceeds according to the equation.

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[1] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co.; Inc., New York, 1934.

[2] A. L. Klebanskii and I. M. Dolgopol'skii, *J. Applied Chem. (U.S.S.R.)*, 1934, 7, 790; *Brit. Chem. Abs.* A, 1935, 193; *Chem. Abs.*, 1935, **29**, 2509. See also V. V. Kedrinskii and E. D. Sabelnikov, *Trans. VI Mendeleev Congr., Theoret. Applied Chem.* 1932, 1935, **2** (Pt. 1) 724; *Chem. Abs.*, 1936, **30**, 2174.

[3] F. A. Weihe, Jr., U. S. P. 2,047,811, July 14, 1936, to McAleer Mfg. Co.; *Chem. Abs.*, 1936, 30, 6006.

[4] A. S. Bernoulli and W. Kambli, *Helv. Chim. Acta*, 1933, 16, 1187; *Chem. Abs.*, 1934, **28**, 1329; *Brit. Chem. Abs.* A, 1934, 36.

$$BrCH_2—CH_2Br + NaOH \longrightarrow CH_2{=}CHBr + H_2O + NaBr.$$

The reaction velocity, however, was considerably reduced by the addition of water. It also varied with temperature in accordance with the expression:

$$k_{t_1} = k_{t_0}e^{r(t_1-t_0)}$$

where k_{t_1} and k_{t_0} are the reaction constants at the new temperature, t_1, and the original temperature, t_0 respectively, r is a constant and e is 2.71828 (the base of the natural logarithms). The value of k_{t_1} was not affected by the presence or absence of water.

Other methods have been proposed for hydrolysis of ethylene dichloride. Askenasy and Heller,[5] for example, used barium carbonate, water and the dihalogen derivative. The mixture was heated between 160°C. and 180°C. for less than an hour (0.5 to 0.75 hour) to give 75 per cent yields of glycol together with 12 per cent of acetaldehyde. The latter was recovered from the vapors which were removed from the autoclave during the reaction. Any higher boiling substances removed in this manner, such as the glycol or dihalide, are returned to the reaction. Another procedure is to mix ethylene dichloride with water to form a constant boiling mixture and conduct the latter over a bed of a water-insoluble carbonate, such as calcium carbonate.[6] The temperature of the reaction chamber (Fig. 134) is maintained at 160-170°C. by superheated steam. The vapor products of the hydrolysis are led to a separator where unreacted ethylene dichloride is removed from glycol. The former may be recycled.

In contrast to the results obtained by other workers, Wada and Sato[7] obtained only 43 per cent glycol by saponifying ethylene dichloride. By hydrolysis of ethylene chlorohydrin at 150°C. and 17 atmospheres pressure, however, they secured 71 per cent yields of glycol. These results confirmed the conclusion of Takahashi and Makishima[8] that hydrolysis of the dihalide gave poorer yields than did that of the chlorohydrin. The procedure of the latter investigators was to treat ethylene dichloride or halohydrin for 10 hours with aqueous sodium carbonate at normal pressures and at temperautres between 60° and 80°C.

Dunstan and Birch[9] have suggested that glycol may be prepared from chlorohydrin in a continuous manner. The chloroethanol in aqueous solution is heated between 105° and 150°C. under pressure with a non-caustic alkali such as sodium carbonate. Ethylene oxide may form to a limited extent only. Lewis[10] recommends that the hydrolysis be carried out in steps as shown in the diagram (Fig.

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[5] P. Askenasy and A. Heller, U. S. P. 1,928,240, Sept. 26, 1933; *Brit. Chem. Abs.* **B**, 1934, 750; *Chem. Abs.*, 1933, **27**, 5756.

[6] R. de M. Taveau, U. S. P. 2,041,272, May 19, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 4512. British P. 424,159, 1935, to Societé Carbochimique Soc. anon.; *Chem. Abs.*, 1935, **29**, 4381; *Brit. Chem. Abs.* **B**, 1935, 395. French P. 774,186, 1934; *Chem. Abs.* 1935, **29**, 2180. See also, P. Ferrero and C. Vandendries, *15me Congr. chim. ind.* (*Bruxelles, Sept. 1935*), **1936**, 250; *Chem. Abs.*, 1936, **30**, 5556.

[7] N. Wada and M. Sato, *J. Soc. Chem. Ind., Japan*, 1935, **38**, Suppl. binding 497; *Chem. Abs.*, 1936, **30**, 1028; *Brit. Chem. Abs.* **B**, 1936, 137.

[8] S. Takahashi and G. Makishima, *J. Soc. Chem. Ind., Japan*, 1935, **38**, Suppl. binding 425, *Chem. Abs.*, 1935, **29**, 7943; *Brit. Chem. Abs.* **B**, 1935, 1035.

[9] A. E. Dunstan and S. F. Birch, U. S. P. 1,996,193, April 12, 1935, to Anglo Persian Oil Co., Ltd.; *Chem. Abs.*, 1935, **29**, 3354. See also French P. 725,150; *Chem. Abs.*, 1932, **26**, 4827. British P. 365,589, 1933; *Chem. Abs.*, 1933, **27**, 1896; *Brit. Chem. Abs.* **B**, 1932, 494. German P. 590,578, 1933; *Chem. Abs.*, 1934, **28**, 3418.

[10] H. A. Lewis, U. S. P. 1,895,517, Jan. 31, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, **27**, 2455; *Brit. Chem. Abs.* **B**, 1933, 904. Canadian P. 359,058, 1936; *Chem. Abs.* 1936, **30**, 6006.

135) but at normal pressure. For example, the chlorohydrin and alkali are united in the mixing kettle (1). The temperature is so low (room temperature) that no reaction takes place, but the mixture passes by gravity feed through each of the kettles 2, 3, 4, and 5. These kettles are heated to progressively higher temperatures and agitated so that the saponification proceeds more readily in the latter than the first kettles. The temperatures in kettles 2, 3 and 4 may, for example, be maintained at 140 to 160°F., 170 to 180°F. and 200-210°F. respectively, and in kettle 5 the mixture is at its boiling point. The vapors from all the kettles are scrubbed to recover organic substances such as olefin oxides or chlorohydrins. The washings are returned to the mixing kettle (1).

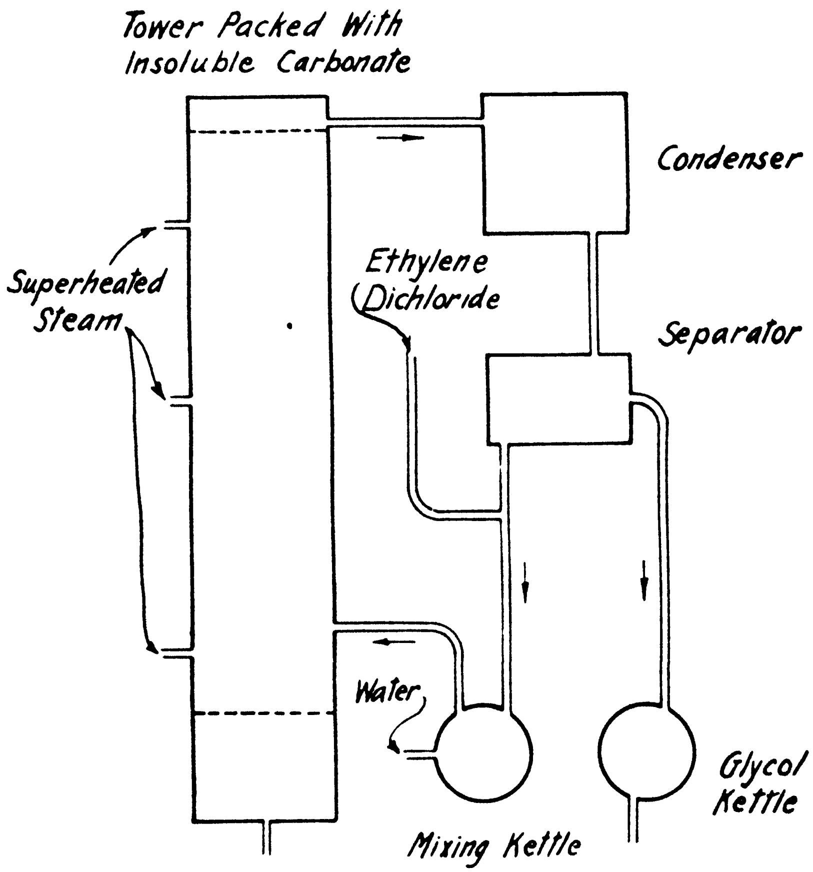

FIG. 134.—Sketch of Equipment for Hydrolysis of Ethylene Dichloride to Ethylene Glycol. (R. de M. Taveau)

In addition to the methods for the hydroxylation of olefins which were mentioned earlier,[11] Skärblom[12] has proposed the interaction of ethylene, water and oxygen carried out in the presence of iodine or its compounds at about 100°C. and under superatmospheric pressures.

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[11] For a discussion, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[12] K. E. Skärblom, U. S. P. 1,982,545, Nov. 27, 1934; *Chem. Abs.*, 1935, 29, 481. Cf. French P. 722,000, 1931; *Chem. Abs.*, 1932, 26, 4067. German P. 561,049, 1932; *Chem. Abs.*, 1933, 27, 1012. German P. 619,195, 1935; *Chem. Abs.*, 1936, 30, 492.

PROPERTIES OF ETHYLENE GLYCOL

Ethylene glycol is a colorless, viscous[13] liquid with a sweet taste. It is completely miscible with water and, in fact, strongly hygroscopic. At 760 mm. pressure it boils at 197.2°C.[14] The density (at 20°C. referred to water at 4°C.) is 1.1140.

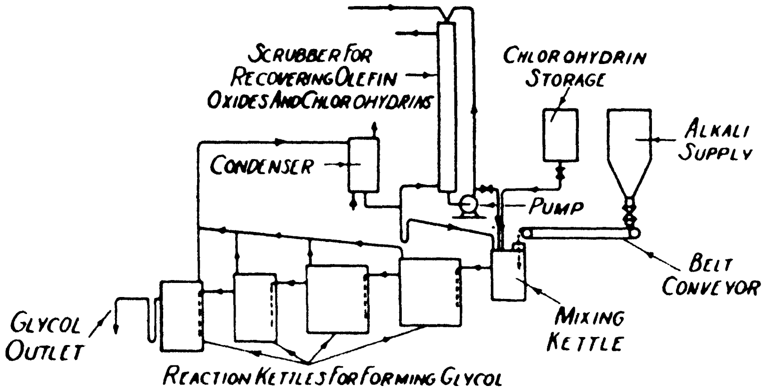
Scrubber For Recovering Olefin Oxides And Chlorohydrins
Chlorohydrin Storage
Alkali Supply
Condenser
Pump
Belt Conveyor
Mixing Kettle
Glycol Outlet
Reaction Kettles For Forming Glycol

FIG. 135.—Flow Diagram for Stepwise Hydrolysis of Ethylene Chlorohydrin. (H. A. Lewis)

The refractive index for the yellow sodium (D) lines is 1.43192 at 20°C. and 1.43172 at 25°C. The vapor pressure, p, is given by the equation

$$\log_{10} p = \frac{A}{T} + B$$

where T is the temperature in degrees absolute and A and B are constants whose values depend somewhat upon the temperature. Between 90° and 130°C. the values are 3193.6 and 9.7423, respectively, whereas between 130° and 197.2°C. they are 2994.2 and 9.2477, respectively.

Romstatt[15] has investigated the densities and refractive indices at different temperatures as well as initial boiling points of aqueous mixtures of glycol. The heat of dilution at 15°C. and the contraction of volume[16] were also measured. Some of Romstatt's results are given in Table 114.

The vapor pressures of ethylene glycol and water mixtures have been ascertained by Trimble and Potts,[17] and also the composition of liquid and vapor phases.

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[13] For the absolute and relative viscosities, see, for example, A. Noll and F. Bolz, *Papier Fabr.*, 1935, **33**, *Tech. Teil* 193; *Chem. Abs.*, 1935, **29**, 6483.

[14] O. J. Schierholtz and M. L. Staples, *J.A.C.S.*, 1935, **57**, 2709; *Chem. Abs.*, 1936, **30**, 1624; *Brit. Chem. Abs.* **A**, 1936, 279. Cf. Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. See also, W. Hieber and A. Woerner, *Z. Elektrochem.*, 1934, **40**, 252, 256; *Chem. Abs.*, 1934, **28**, 5324; *Brit. Chem Abs* **A**, 1934, 836. V. A. Kireev and A. A. Popov, *J. Applied Chem.* (*U.S.S.R.*), 1934, **7**, 489; *Chem. Abs.*, 1935, **29**, 2061.

[15] G. Romstatt, *Industrie Chimique*, 1935, **22**, 648; *Chem. Abs.*, 1936, **30**, 372. See also D. S. Davis, *Chem. Analyst*, 1935, **24** (2) 8; *Chem. Abs.*, 1935, **29**, 5707.

[16] This is the phenomenon observed on dilution of many substances. For example, 50 cc. each of water and absolute ethanol when mixed give 98 cc. of dilute alcohol.

[17] H. M. Trimble and W. Potts, *Ind. Eng. Chem.*, 1935, **27**, 66; *Brit. Chem. Abs.* **A**, 1935, 290; *Chem. Abs.*, 1935, **29**, 1694.

TABLE 114.—*Ethylene Glycol—Water Mixtures.*

Glycol % by Weight	Density at 0°C.	Weight of Glycol in 1 Liter Solution at 15°C. Grams.	Density at: 15°C.	30°C.	45°C.	Refractive Index at: 15°C.	30°C.	45°C.	Initial Boiling Point, °C.
0	0.9998	—	0.9991	0.9957	0.9902	—	–	—	99.5°
5	1.0078	50.30	1.0051	0.9999	0.9910	1.3383	1.3373	1.3358	100°
10	1.0148	101.21	1.0125	1.0056	0.9949	1.3423	1.3418	1.3403	100.5°
15	1.0223	152.75	1.0190	1.0116	1.0001	1.3473	1.3463	1.3443	101°
20	1.0303	205.33	1.0260	1.0186	1.0060	1.3523	1.3513	1.3493	101.5°
25	1.0380	258.26	1.0333	1.0245	1.0126	1.3583	1.3568	1.3538	102.5°
35	1.0537	366.11	1.0470	1.0372	1.0238	1.3682	1.3667	1.3633	105°
50	1.0755	534.18	1.0675	1.0561	1.0416	1.3842	1.3812	1.3782	108°
60	1.0885	649.35	1.0808	1.0673	1.0528	1.3952	1.3917	1.3892	111°
75	1.1064	822.36	1.0968	1.0828	1.0674	1.4101	1.4061	1.4031	117°
85	1.1152	940.26	1.1045	1.0922	1.0763	1.4191	1.4161	1.4126	126°
Pure Glycol	1.1257	1116.50	1.1165	1.1032	1.0867	1.4335	1.4306	1.4261	195°

A modified Othmer still (Fig. 136) was employed for obtaining the vapor phase, the analysis being made refractometrically. The vapor pressure was expressed by the equation

$$\log_{10}p = A + \frac{B}{T},$$

where T is absolute temperature and p the vapor pressure. A and B are constants whose values depend upon the composition of the liquid.[18] The ratio of glycol in vapor and liquid varies only slightly with pressure, although it changes markedly with change in composition of the liquid. Some of the results, together with the values computed for A and B in the above equation, are given in Table 115.

TABLE 115.—*Ethylene Glycol: Composition—Boiling Point Relations.*

Glycol in Liquid		Pressure = 228 mm. Glycol in Vapor			Pressure = 430 mm. Glycol in Vapor			Pressure = 603 mm. Glycol in Vapor			Pressure = 747 mm. Glycol in Vapor			Values of Constants in Equation	
%	Mol Fraction	B.P. °C.	%	Mol Fraction	B.P. °C.	%	Mol Fraction	B.P. °C.	%	Mol Fraction	B.P. °C.	%	Mol Fraction	A	$-B$
0	0.0	69.5	...	...	85.0	...	..	93.7		.	99.6		...	8.7120	2178
10	0.03	70.6	..	...	85.4	..	...	94.3	0.1	.	100.9	0.1	...	8.7000	2182
20	0.07	71.5	0.2	...	86.3	0.2	...	95.7	0.2	.	102.0	0.2	..	8.6900	2185
30	0.11	72.7	0.3	...	87.4	0.3	.	97.1	0.3	..	103.4	0.3	.	8.6800	2188
40	0.17	74.0	0.7	...	89.0	0.7	.	99.0	0.7		105.5	0.7		8.6700	2190
50	0.23	76.1	1.0	0.002	91.1	1.2	0.002	101.3	1.2	0.002	108.0	1.2	0.002	8.6690	2201
60	0.31	78.9	2.0	0.003	94.1	2.3	0.004	104.2	2.3	0.004	111.2	2.3	0.004	8.6640	2220
70	0.40	83.1	3.4	0.010	99.0	4.6	0.012	108.7	4.7	0.013	116.7	4.9	0.013	8.6680	2250
80	0.54	89.6	6.6	0.020	106.1	9.0	0.028	115.4	9.4	0.030	124.1	9.7	0.031	8.6730	2293
90	0.73	103.1	17.3	0.06	120.0	20.7	0.072	130.2	21.3	0.076	138.7	22.2	0.080	8.7000	2386
95	0.85	118.4	33.4	0.13	135.0	38.8	0.16	145.8	39.7	0.16	154.0	41.3	0.17	8.8000	2528
97	0.90	128.0	48.8	0.22	145.7	53.6	0.26	156.0	53.2	0.25	164.3	55.7	0.27	8.9000	2632
98	0.93	134.7	59.0	0.30	152.6	63.2	0.34	163.4	63.7	0.34	171.3	65.3	0.36	8.9500	2694
99	0.97	145.0	75.4	0.47	163.0	77.6	0.50	173.4	78.2	0.51	182.0	79.8	0.53	9.0250	2800
100	1.00	160.7	100.0	1.00	179.3	100.0	1.00	190.0	100.0	1.00	196.7	100.0	1.00	9.1580	2952

Chemically, ethylene glycol behaves as an alcohol. It may be oxidized, for example, electrochemically at a smooth platinum anode,[19] to give an hydroxyaldehyde. Its homolog, propene glycol, as well as phenylethylene glycol, under similar conditions give the corresponding hydroxy ketones. Another reaction of electrochemical oxidation is splitting a primary or secondary glycol such as ethylene or 2,3-butene glycol into two aldehyde molecules. A ditertiary glycol, such as pinacol, will be oxidized to two ketone molecules by this reaction. These latter reactions are more pronounced at higher potentials.

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[18] It will be seen that A corresponds to the B of Schierholtz and Staples (*loc. cit.*), while −B corresponds to their A.

[19] E. Tommila, *Ann. Acad. Sci. Fennicae*, 1934, **39**, 3; *Chem. Abs.*, 1935, **29**, 2093.

Concentrated hydrochloric acid (hydrous medium) converts ethylene glycol into the chlorohydrin or dichloride, whereas hydrogen chloride (anhydrous medium) appears to form first the epoxide (ethylene oxide) and subsequently the chloro compounds.[20]

According to Kedrinskii and Skornyakova[21] solutions containing ethylene and propene glycol should be analyzed by oxidation with dichromate as well as by density and water determinations. If salt is also present it may be estimated by the Vollrath method (see Chapter 50).

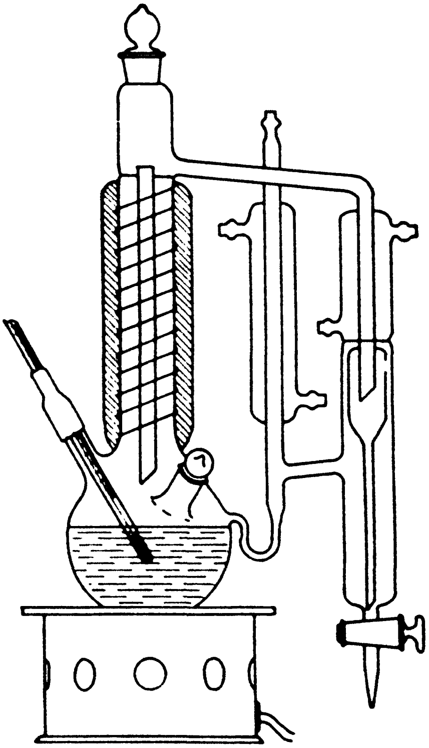

FIG. 136.
Modified Othmer Still for Vapor Analysis.
(H. M. Trimble and W. Potts)

Courtesy Industrial and Engineering Chemistry

TOXICITY OF ETHYLENE GLYCOL

There is considerable difference of opinion as to the possibility of the exhibition of poisonous properties by glycol.[22] The evidence appears to be that its toxicity depends very largely upon the conditions under which it is tested. Mancini,[23] for example, has observed that the minimum lethal dose is from 3 to 9 cc. per kilogram of body weight depending upon the experimental animal used. He stated that it could be administered in reasonable doses without fear of toxic action. Injections intramuscularly are said to cause neither persistent pain, irritation or abscess. Applications to the mucosa cause a slight disturbance, whereas there is no effect when applied to the skin. The possible objectionable results are hemolysis (cf. Chapter 53), oxaluria[24] and decrease in blood pressure. Wiley, Hueper and van Oettingen[25] have pointed out that concentrations of glycol as high as 300 mg. per 1000 liters of air have no toxic effects on rats or mice, and probably would have none on man. A concentration of 0.5 mg. per 1. is saturated. Brown[26] has also directed attention to the toxicity of both glycol and dioxane.[27]

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[20] H. H. Schlubach, H. Elsner and H. Knoop, *Angew. Chem.*, 1934, 47, 130; *Brit. Chem. Abs.* A, 1934, 396. See also Carleton Ellis, *loc. cit.*

[21] V. V. Kedrinskii and V. F. Skornyakova, *Materials on Cracking and Chemical Treatment of Products Obtained, Khimteoret (Leningrad)*, 1935, No. 2, 201; *Chem. Abs.*, 1935, 29, 5775; *Brit. Chem. Abs.* B, 1936, 536.

[22] See, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[23] M. A. Mancini, *Arch. fisiol.*, 1935, 35, 157; *Chem. Abs.*, 1936, 30, 4928. *Boll. soc. ital. biol. sper.*, 1935, 10, 964; *Chem. Abs.*, 1936, 30, 2640.

APPLICATIONS OF ETHYLENE GLYCOL

Ethylene glycol has found use in many fields.[28] It has been employed as an antifreeze in automobile cooling systems and also as a preservative. It is a solvent for many organic substances in which respect it resembles ethanol. Thus Rae[29] has obtained a strongly tinctorial extract from cudbear (a lichen), and from other natural sources such as saffron, red rose petals, Brazil wood, carmine, buttercups and *Centaurea montana* (a blue-flowered plant native to the Pyrenees). In most cases the presence of water was harmful, but deeper tints were obtained from madder and henna in the presence of water than without it. Glycol could not be used for preparing extracts of litmus, alkanet root or gamboge. The glycol has been proposed as a solvent for insecticidal compositions containing pyrethrins.[29a] Ethylene glycol (5 per cent by volume) has been suggested as a selective solvent for the more readily oxidizable constituents of gasoline (cf. Chapter 40), thus reducing the gum- and color-forming tendency of the fuel.[30] Dehydration of diethyl ether may be effected by mixing the latter with 20 to 50 volume per cent of glycol and distilling. The ether is said to contain less than 0.6 per cent water after this treatment. Other substances which are hygroscopic and do not form azeotropic mixtures with ether may also be used, such as propene glycol, diethylene glycol, glycerol, and triethanolamine.[31]

Lockspeiser[32] has suggested that glycol be used either alone, or with 10 per cent ethanol to prevent the formation of ice on airplane propellers during flight. In experimental tests on a Hart and a Gordon airplane, 1.5 and 1.7 pints of liquid were used per hour, respectively. Milliken[33] reported, as a further application of glycol, that it is possible to reduce the viscosity of nitrocellulose by digestion with glycol or glycerol (of 95% or more concentration) at 160°C. and atmospheric pressure. According to Blount and Boardman,[33a] a soluble oil may be prepared by mixing 14 parts sodium soaps (e.g. those from corn-oil acids), 6 parts water, 64 parts mineral oil, 10 parts water-white rosin, 4 parts of a polyhydric alcohol (such as glycol or diethylene glycol) and 2 parts of a monoalkylated dihydric alcohol such as ethylene glycol monoethylether.

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[24] The presence of oxalic acid in the urine.

[25] F. H. Wiley, W. C. Hueper and W. F. v. Oettingen, *J. Ind. Hyg. Toxicol*, 1936, **18**, 123; *Chem. Abs.*, 1936, **30**, 2638.

[26] C. L. M. Brown, *Quart. J. Pharm. Pharmacol.*, 1935, **8**, 390; *Chem. Abs.*, 1936, **30**, 1943.

[27] For a discussion of dioxane, see Chapter 23.

[28] See, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

[29] J. Rae, *Pharm. J.*, 1933, **131**, 369; *Chem. Abs.*, 1933, **27**, 5893.

[29a] J. Ripert, U. S. P. 2,074,188, March 16, 1937, to Le Fly Tox.

[30] G. McIntyre and E. G. Ulbricht, U. S. P. 1,985,613, Dec. 25, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 1241; *Brit. Chem. Abs.* **B**, 1935, 1128.

[31] P. S. Greer, U. S. P. 1,974,069, Sept. 18, 1934, to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1935, 761; *Chem. Abs.*, 1934, **28**, 6727.

[32] B. Lockspeiser, *Aircraft Eng.*, 1935, 7, 278; *Chem. Abs.*, 1936, **30**, 786.

[33] M. G. Milliken, U. S. P. 1,957,180, May 1, 1934, to Hercules Powder Co.; *Brit. Chem. Abs.* **B**, 1935, 266; *Chem. Abs.*, 1934, **28**, 4231.

[33a] A. L. Blount and D. W. Boardman, U. S. P. 1,965,935, July 10, 1934, to Union Oil Co. of Calif.; *Brit. Chem. Abs.* **B**, 1935, 485; *Chem. Abs.*, 1934, **28**, 5684. See also French P. 789,626, 1935, to International Hydrogenation Patents, Ltd.; *Chem. Abs.*, 1936, **30**, 1989.

Tatter[34] has suggested that a mixture containing 50 volume per cent glycol together with water (37 to 45 per cent) and a sulphonated oil (13 to 5 per cent) be used as the hydraulic fluid in brakes. Other compositions intended for this same purpose comprise the dihydric alcohol mixed with the sodium salt of the sulphuric ester of castor oil,[34a] with furfurol or other furan derivatives,[34b] or with lard oil (containing 10 to 15 per cent free fatty acids) and a large proportion of ethanolamines (40 to 100 per cent of the weight of the lard oil).[34c] Cox[35] proposed a mixture of ethylene and propene glycols, or other polyhydric alcohols, as a heat or pressure transfer medium. Furthermore, according to Cox and Clapsadle[36] a mixture of 60 to 30 per cent ethylene and 40 to 70 per cent diethylene glycols may be used as a heat transfer medium in cooling systems and as a pressure transfer medium in hydraulic brakes.

Glycol (95 per cent) has been recommended as an antifreeze in conjunction with 5 per cent or less of a mixture containing ethanolamine salts of fatty acids.[37] It has also been suggested as an absorptive liquid for ammonia,[38] as a solvent for extracting colored substances from rosin,[39] together with an oil as a vehicle for an abrasive containing bentonite,[40] and for addition to solid carbon dioxide to decrease the size of crystals and thereby improve its mechanical properties.[41] An interesting application of ethylene glycol is as the electrolyte for a battery.[42] The cell contains two electrodes, one of aluminum, magnesium, beryllium, cadmium, zinc or an alloy or amalgam of these or of chromium, silver or silver plated metals, and the other of cuprous, ferric, vanadic, plumbic or cadmic oxide, sulphide or selenide, or carbides of iron or nickel. The electrolyte consists of ethylene glycol, glycerol or a derivative of one of these to which has been added a small proportion of a weak organic acid such as lactic, malic or tartaric. A battery of this type is said to be particularly applicable for maintaining a grid-bias on a vacuum tube (a so-called "c-battery").

Esters of Ethylene Glycol

The esters of glycol have been the subject of many investigations.[43] The dinitrate is used extensively in admixture with nitroglycerine to form explosives which have lower freezing points and less susceptibility to shock than glycerol trinitrate itself. Nitration is carried out in much the same manner as in the preparation of nitroglycerine. A modification proposed by Brown[44] comprises the control of the reaction temperature by addition of a hydrocarbon which is unaffected by the nitrating mixture, and which is volatilized by the heat of reaction. Isopentane was suggested as fulfilling the requirements.

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[34] J. W. Tatter, U. S. P. 1,928,956, Oct. 3, 1933, to Lewis Differential Co.; *Brit. Chem. Abs.* **B**, 1934, 610; *Chem. Abs.*, 1933, **27**, 5910.

[34a] E. Muench and F. Nicolai, U. S. P. 1,898,564, Feb. 12, 1933, to I. G. Farbenind. A.-G., *Chem. Abs.*, 1933, **27**, 2772. *Cf.* British P. 333,200, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, **25**, 567; *Brit. Chem. Abs.* **B**, 1930, 1051.

[34b] German P. 548,003, 1931, to Hydraulic Brake Co.; *Chem. Abs.*, 1932, **26**, 3634.

[34c] L. D. Dana and C. W. Georgi, U. S. P. 1,988,584, Jan. 22, 1935, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, **29**, 1543; *Brit. Chem. Abs.* **B**, 1936, 90.

[35] H. L. Cox, U. S. P. 2,003,429, June 4, 1935, to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1936, 672; *Chem. Abs.*, 1935, **29**, 4857.

[36] H. L. Cox and L. J. Clapsadle, U. S. P. 2,003,662, June 4, 1935, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, **29**, 4857; *Brit. Chem. Abs.* **B**, 1936, 399.

[37] L. I. Dana and C. W. Georgi, U. S. P. 1,988,584, Jan. 22, 1935 to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, **29**, 1543; *Brit. Chem. Abs.* **B**, 1936, 90. Canadian P. 355,319, 1936; *Chem. Abs.*, 1936, **30**, 2287. See also H. L. Cox, U. S. P. 2,042,830, June 2, 1936, to Union Carbide and Carbon Corp.; *Chem. Abs.*, 1936, **30**, 4956.

[38] R. S. Taylor, U. S. P. 1,914,222, June 13, 1933, to Electrolux Servel Corp.; *Brit. Chem. Abs.* **B**, 1934, 304; *Chem. Abs.*, 1933, **27**, 4325.

[39] I. W. Humphrey, U. S. P. 1,890,086, Dec. 12, 1932, to Hercules Powder Co.; *Brit. Chem. Abs.* **B**, 1933, 756; U. S. P. 1,905,173, April 25, 1933; *Chem. Abs.*, 1933, **27**, 3628; *Brit. Chem. Abs.* **B**, 1934, 28.

[40] H. C. Fuchs, U. S. P. 2,006,162, June 25, 1935, to Permatex Co., Inc.; *Chem. Abs.*, 1935, **29**, 5552; *Brit. Chem. Abs.* **B**, 1936, 643.

[41] C. L. Jones, U. S. P. 2,020,189, Nov. 5, 1935, to Adico Development Corp., *Chem. Abs.*, 1936, **30**, 335.

[42] British P. 427,098, 1935, to P. R. Mallory & Co., Inc.; *Chem. Abs.*, 1935, **29**, 6154; *Brit. Chem. Abs.* **B**, 1935, 508.

[43] See Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, 1934.

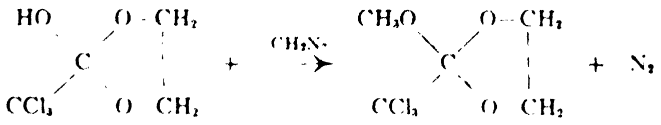
There are three general methods which have been employed for the preparation of the glycol mono- and di-esters of aliphatic acids. These are:

a. Reaction of salts of acids with ethylene dihalides.
b. Esterification of glycol with acids or their anhydrides.
c. Condensation of epoxides with acids or anhydrides.

For example, glycol diacetate may be prepared by any of these three methods. Thus, it has been synthesized in 20 per cent yield by passing vapors of glycol and acetic acid in a stream of nitrogen over active carbon containing small amounts of phosphoric acid.[45] Although better yields were secured at 130° to 150°C., it was found necessary to work with temperatures of 160° to 170°C. to obtain a satisfactory reaction velocity. The only product from this procedure was the diacetate whether one or two moles of acetic acid were used per mole of glycol. The monoacetate, which may be employed as a component of a fluid for hydraulic brakes,[46] may be prepared by the esterification of either the glycol or ethylene oxide (epoxide).

The aliphatic esters have found employment in various ways, particularly as solvents. Dreyfus[47] proposed that a diester of glycol be decomposed by heating between 450° and 600°C. with the formation of an acid anhydride. In this manner ethylene glycol diacetate is reported to be converted into acetic anhydride. Isobutyrates of glycol or diethylene glycol are reported to be plasticizers for cellulose acetate.[48] The glycol derivatives of saturated or unsaturated fatty acids such as glycol stearate have been suggested as ingredients for soap-free shaving preparations.[49] On the other hand, Lomakin and Smirnov[50] have proposed as a lubricant the products resulting from esterification of bone grease with ethylene glycol at temperatures below 130°C. Adams[51] recommended the ethylene and propene glycol esters of branched-chain aliphatic acids of 12 to 20 carbon atoms as bactericides and bacteriostatic agents.

The work of Meerwein and Sönke[52] on the trichloroacetates is of interest. These investigators prepared trichloroacetyl glycol from ethylene oxide and trichloroacetic acid. Because of its strongly acid nature and vigorous reaction with diazomethane, they believed that the compound was an ortho-ester:



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[44] B. K. Brown, U. S. P. 1,973,559, Sept. 11, 1934, to Standard Oil Co. of Ind; *Brit. Chem. Abs.* **B**, 1935, 761; *Chem. Abs.*, 1934, **28**, 6727.

[45] M. B. Turova-Pollak and V. F. Dzioma, *J. Applied Chem. (U.S.S.R.)*, 1936, **9**, 696; *Chem Abs.*, 1936, **30**, 7540; *Brit. Chem. Abs.* **A**, 1936, 821.

[46] A. T. K. Tseng, U. S. P. 1,990,149, Feb. 5, 1935, to Hydraulic Brake Co; *Brit. Chem. Abs.* **B**, 1935, 1078; *Chem. Abs.*, 1935, **29**, 1908.

[47] H. Dreyfus, U. S. P. 2,050,287, Aug. 11, 1936; *Chem. Abs.*, 1936, **30**, 6765.

[48] E. F Izard, U. S. P. 2,014,381, Sept. 17, 1935, to DuPont Viscoloid Co.; *Brit. Chem. Abs.* **B**, 1936, 1109; *Chem. Abs.*, 1935, **29**, 7528.

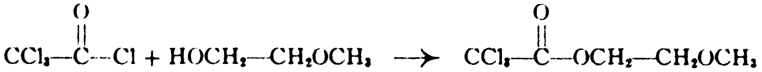
[49] F. Heckt, O. Hall and G. Marchant, German P. 604,774, 1934; *Chem. Abs.*, 1935, **29**, 892.

[50] G. A. Lomakin and V. N. Smirnov, Russian P. 35,311, 1934; *Chem. Abs.*, 1935, **29**, 8321.

[51] R. Adams, U. S. P. 1,917,681, July 11, 1933, to Abbott Laboratories; *Chem. Abs.*, 1933, **27**, 4539; *Brit. Chem. Abs.* **B**, 1934, 428.

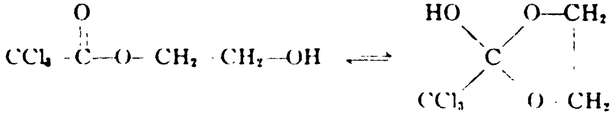
[52] H. Meerwein and H. Sönke, *Ber.*, 1931, **64B**, 2375; *Chem. Abs.*, 1932, **26**, 87; *Brit. Chem Abs.* **A**, 1931, 1395. *J. prakt. Chem.*, 1933, **137**, 295; *Brit. Chem. Abs.* **A**, 1933, 1273; *Chem. Abs.*, 1933, **27**, 4215. See also H. Meerwein and G. Hinz, *Ann.*, 1930, **484**, 1; *Brit. Chem. Abs.* **A**, 1931, **206**; *Chem. Abs.*, 1931, **25**, 1484.

As a confirmation of this structure, the straight-chain trichloroacetyl glycol methyl ether was made from trichloroacetyl chloride and 2-methoxyethanol.



$$CCl_3{-}\overset{O}{\overset{\|}{C}}{-}Cl + HOCH_2{-}CH_2OCH_3 \longrightarrow CCl_3{-}\overset{O}{\overset{\|}{C}}{-}OCH_2{-}CH_2OCH_3$$

The product was very different in chemical properties from the supposed ortho-ester. For example, alcoholysis (by heating with alcohol) of the ortho-ester resulted in replacement of the methyl group by another alkyl residue, whereas the straight-chain compound should give 2-methoxyethanol and an alkyl trichloroacetate. Further experiments on the reactions of ethyleneglycol-monotrichloroacetate (such as with ammonia, acetyl or thionyl chloride) showed that it was a tautomeric mixture (in uncertain proportions) of the two possible compounds having the structures:



2-hydroxyethyl trichloroacetate — *2-hydroxy-2-trichloromethyl 1,3-dioxolane.*

In this connection, Hibbert and Greig[53] investigated the nature of the product obtained in endeavoring to prepare glycol trichloroacetates. They also reported a compound with a dioxolane structure, which was said to decompose on heating at 100° to 110°C. to give ethylene carbonate and chloroform. This result, however, was not confirmed by Meerwein and Sönke. The physical properties of some of the 2-alkoxy-2-trichloromethyl-1,3-dioxolanes prepared by these latter workers are given in Table 116.

TABLE 116.—*Properties of 2-Alkoxy-2-trichloromethyl-1,3-dioxolanes.*

Alkyl Group	Boiling Point Pressure	Boiling Point Temperature	Density at 20° 4°	Index of Refraction n_D^{20}
Methyl (m. p., 78-8.5°)	10 mm.	112-3°C.	1.486	1.45652 (n_D^{100})
Ethyl (m. p., 26.4°)	10 mm.	119-20°C.	1.429	1.47846
Propyl	2.1 mm.	99°C.	1.370	1.47635
Butyl	5.85 mm.	125.5°C.	1.321	1.47439

GLYCOL ESTERS OF POLYCARBOXYLIC ACIDS

The esters of polyhydric alcohols and polybasic acids are well known to exhibit a resinous character because of the tendency to form very large molecules.[54] On the other hand many of the simpler esters of glycol are said to be plasticizers. For example, Gabriel and Swallen[55] obtained a neutral product by the interaction of phthalic anhydride and ethylene glycol, using sulphuric acid as a catalyst. The product may be used as a plasticizer with nitrocellulose. Nonresinous esters of dibasic acids and polyhydroxy compounds may be synthesized from the alcohol and acid anhydride by reacting them in the presence of a tertiary organic base. By employing one mole equivalent of base for the corresponding amount of acid anhydride, it is possible to obtain acid esters of polyhydric alcohols,[56] which may be reacted further with monohydric alcohols or partially esterified cellulose. Dreyfus[57] has suggested that hydroxyalkyl alkoxyalkyl esters of polycarboxylic acids such as:

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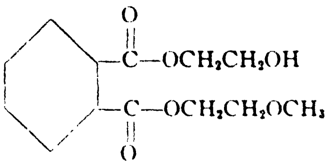
[53] H. Hibbert and M. E. Greig, *Can. J. Research*, 1931, 4, 254; *Chem. Abs.*, 1931, 25, 2973

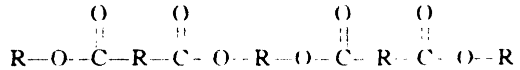
[54] See Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[55] C. L. Gabriel and L. C. Swallen, U. S. P. 1,946,202, Feb. 6, 1934, to Commercial Solvents Corp.; *Chem. Abs.*, 1934, 28, 2372; *Brit. Chem. Abs.* B, 1934, 1003.

[56] French P. 761,591, 1934, to Kodak-Pathé; *Chem. Abs.*, 1934, 28, 4432.

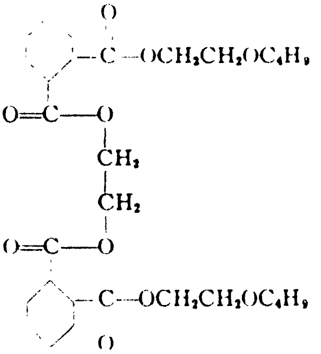


be used as plasticizers. Frazier[58] suggested the preparation of esters of the type



$$R{-}O{-}\overset{\overset{O}{\|}}{C}{-}R{-}\overset{\overset{O}{\|}}{C}{-}O{-}R{-}O{-}\overset{\overset{O}{\|}}{C}{-}R{-}\overset{\overset{O}{\|}}{C}{-}O{-}R$$

by heating 2 moles of a polycarboxylic acid such as phthalic ($HO{-}CO{-}R^1{-}CO{-}OH$) with 1 mol of a glycol ($HO{-}R''{-}OH$) such as an alkene or polyalkene glycol and subsequently esterifying with a monohydric alcohol ($R{-}OH$). An example of a product of the kind is di-β-butoxyethyl ethyleneglycol diphthalate,



Ethers of Ethylene Glycol

Of about equal importance with the esters of glycol are the ethers and their derivatives which have been employed in numerous instances as solvents and diluents. For example, glycol monoethyl ether has been used in duplicator fluid together with water and ethanol for wetting the wax impressions prior to printing.[59] Mixtures of this ether with castor oil and alkyl derivatives of toluene sulphonamide[59a] are suggested as fluids for hydraulic brakes. North[60] has employed the oleates of glycol methyl- and butylethers as plasticizers. On the other hand, Seymour[61] employed the formals of ethylene, propene or diethylene glycol or glycerol monochlorohydrin as solvents for cellulose derivatives and in binding layers of cellulosic materials. The products were formed by heating the glycol with formaldehyde (or its polymers) in the presence of an acid condensing agent such as hydrogen chloride, sulphuric or phosphoric acid or ferric chloride.

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[57] H. Dreyfus, British P. 418,506, 1934; *Chem. Abs.*, 1935, **29**, 2260; *Brit. Chem. Abs.* **B**, 1935, 33. See also British P. 438,540, 1934; *Brit. Chem. Abs.* **B**, 1936, 142; *Chem. Abs.*, 1936, **30**, 2757.

[58] R. B. Frazier, British P. 410,797, 1934, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1934, **28**, 6443; *Brit. Chem. Abs.* **B**, 1934, 1094.

[59] P. A. Shillenn, U. S. P. 1,996,125, April 2, 1935, to Radio Corp. of America; *Brit. Chem. Abs.* **B**, 1936, 462; *Chem. Abs.*, 1935, **29**, 3429.

[59a] German P. 624,784, 1936, to Wagner Electrical Corp.; *Chem. Abs.*, 1936, **30**, 4956.

[60] C. O. North, U. S. P. 2,010,560, Aug. 6, 1935, to H. S. Kreighbaum; *Brit. Chem. Abs.* **B**, 1936, 823; *Chem. Abs.*, 1935, **29**, 6607.

[61] G. W. Seymour, U. S. P. 1,990,098, Feb. 5, 1935, to Celanese Corp. of America; *Brit. Chem. Abs.* **B**, 1936, 97; *Chem. Abs.*, 1935, **29**, 1907 U. S. P. 2,031,619, Feb. 25, 1936; *Chem. Abs.*, 1936, **30**, 2208. British P. 424,837, 1935, to British Celanese, Ltd.; *Chem. Abs.*, 1935, **29**, 5125; *Brit. Chem. Abs.* **B**, 1935, 619. Canadian P. 352,701, 1935, to Camille Dreyfus; *Chem. Abs.*, 1935, **29**, 8329. Canadian P. 353,271, 1935, to Camille Dreyfus; *Chem. Abs.*, 1935, **29**, 8329. See also British P. 440,962, 1934, to British Celanese, Ltd.; *Brit. Chem. Abs.* **B**, 1936, 263.

A small proportion (1 part) of monoethyl ether of ethylene glycol has been used together with beeswax (70 parts), stearic acid (20 parts) and paraffin (10 parts) in making wax for molded candles.[62] It has also been employed admixed with *o*-dichlorobenzene and an ether of diethylene glycol, as a solvent for oils during dewaxing by chilling to —23°C.[63] Furthermore, its acetate has been utilized in conjunction with an immiscible liquid (e.g., water) in refrigerating apparatus, the acetate furnishing a liquid medium interspersed between any crystals formed.[64]

The toxicity of the monoethyl ether of ethylene glycol has been investigated.[64a] It was reported that the ether has a relative toxicity of approximately the same order as carbon tetrachloride and benzene, when considering acute poisoning. Further, it was stated that air, saturated at 20°C. with the vapor of the ether, possesses a disagreeable odor and also produces moderate eye irritation. If these properties are heeded as warning of the occurrence of a potentially dangerous atmosphere and exposure is avoided, it is believed that acute poisoning will not occur.

The monoethers, including the butyl ether of glycol, have been suggested for addition (0.1 to 5.0 per cent) to a mineral oil in conjunction with 1.0 to 5.0 per cent of an aluminum soap of stearic, palmitic or behenic acid.[65] Boyle[66] and Neilson[67] have recommended the monobutyl ether of ethylene glycol in compositions intended to clean metals prior to painting. Boyle employs phosphoric acid, the ether (as an oil solvent) and a wetting agent, whereas Neilson used phosphoric acid and saponin (a glucoside) together with an optional amount of the ether. Glycol monoethers have also been advocated as emulsifying assistants for mixtures of soap and benzene, or its homologs, and other hydrocarbon materials[68] and as a solvent in preparing a coating composition from chlorinated rubber and an organic abietate.[69]

The naphthyl ethers of glycol have been synthesized by heating glycols with sodium naphthoxide or with naphthol and sulphuric acid at about 120°C.[70] On the other hand, the benzyl ethers of glycol (and glycerol) may be obtained by heating the polyhydric alcohol with benzyl chloride and powdered sodium hydroxide.[71] In an analogous manner ethers may be made from dodecyl, myristyl, cetyl or oleyl halides, or those of alcohols obtained by reduction of resins, or resinic or naphthenic acids.[72] The ethers of aliphatic polyhydric alcohols may be esterified with aliphatic acids containing more than 7 carbon atoms to give plasticizers, such as 2-ethoxyethyl caprylate.[73] Cyclic acetals may be prepared on condensation of an aldehyde and a polyhydric alcohol by heating with benzene so that water is removed as it forms.[74] Internal ethers of glycol such as dioxane and its isomers are considered more fully in Chapter 23. Glycol dialkyl ethers are said to result on heating a monoalkyl ether either by itself or with a monohydric alcohol in the presence of sulphuric acid.[75]

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[62] L. W. Geller, U. S. P. 1,960,994, May 29, 1934, to Will and Baumer Candle Co.; *Brit. Chem. Abs.* **B**, 1935, 319; *Chem. Abs.*, 1934, **28**, 4620.

[63] B. Y. McCarty and W. E. Skelton, U. S. P. 2,035,490, March 31, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 3630.

[64] J. Fleischer, U. S. P. 1,943,269, Jan. 9, 1934, to Frigidaire Corp.; *Chem. Abs.*, 1934, **28**, 1794; *Brit. Chem. Abs.* **B**, 1934, 816.

[64a] C. P. Waite, F. A. Patty and W. P. Yant, *U. S. Publ. Health Repts.*, 1930, **45**, 1459; *Chem. Abs.*, 1930, **24**, 4849.

[65] A. L. Blount, U. S. P. 2,031,405, Feb. 18, 1936, to Union Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 2363.

[66] C. L. Boyle, Canadian P. 356,078, 1936; *Chem. Abs.*, 1936, **30**, 2669.

[67] H. R. Neilson, U. S. P. 1,935,911, Nov. 21, 1933, to H. E. Westervelt; *Chem. Abs.*, 1934, **28**, 916; *Brit. Chem. Abs.* **B**, 1934, 811.

[68] G. Kropfhammer, German P. 615,563, 1935; *Chem. Abs.*, 1935, **29**, 8182.

[69] W. Koch, U. S. P. 1,957,786, May 8, 1934, to Hercules Powder Co.; *Brit. Chem. Abs.* **B**, 1935, 278; *Chem. Abs.*, 1934, **28**, 4256.

[70] M. A. Dahlen, C. K. Black and W. L. Foohey, U. S. P. 1,979,144; 1,979,145, Oct. 30, 1935, to E. I. du Pont de Nemours & Co., *Chem. Abs.*, 1935, **29**, 177.

[71] S. Danilov, V. Dryakhlitzuina, O. Manokhina and N. Orlova, *Plasticheskie Massui*, **1934**, No. 2, 11; *Chem. Abs.*, 1934, **28**, 6300. S. Danilov, V. Dryakhlitzuina and O. Manokhina, *Rev. gen. mat. plastiques*, 1934, **10**, 365; *Chem. Abs.*, 1935, **29**, 756.

[72] French P. 768,554, 1934, to Henkel & Cie. G.m.b.H.; *Chem. Abs.*, 1935, **29**, 475.

The tertiary ethers of glycol have been prepared by condensation of a tertiary olefin, such as *2*-methyl-butene-*2* or isobutene, with glycol in the presence of sulphuric acid.[76] In this way the mono-*ter*-amyl ether (b.p. 50°-55°C. at 3 mm.) and the various *ter*-butyl ethers listed in Table 117 may be synthesized.

TABLE 117.—*Tertiary Butyl Ethers of Glycol and its Monoalkylethers.*

Alcohol	Boiling Point of the *ter*-Butyl Ether
Ethylene Glycol	152.5°
Glycol methyl ether	131-2°
Glycol ethyl ether	147.5°
Glycol *n*-butyl ether	83.4° (20 mm.)
Glycol *ter*-butyl ether	171°
Propene glycol	151-3°

These ethers and diethers are said to be useful in dyeing, explosives, as lubricants, cooling liquids for internal combustion engines, and as solvents and plasticizers. The esters of glycol ethers and hydroxy acids may be further esterified by acids to give substances which are said to be plasticizers.[77] Alkoxyalkyl esters of polybasic acids such as adipic, sebacic[78] or benzoylbenzoic[79] have been proposed.

POLYETHYLENE GLYCOLS

The formation of an ether by elimination of water (one molecule) from two molecules of glycol leads to the production of diethylene glycol or *2,2'*-dihydroxydiethyl ether. This reaction is assisted by various catalysts, as for example, heating glycol to 190°C. with 0.3 per cent by weight of iodine.[80] Compounds of as high molecular weight as decaethylene glycol (mol. wt. about 458) may be obtained Another procedure involves the interaction of ethylene oxide and glycol. It has been suggested that the dichloride of a polyethylene glycol be condensed with the monosodium salt of a polyethylene glycol. For example, 171 g. diethylene glycol and 100 cc. of ether were treated with 3.5 g. sodium metal until the latter had dissolved. To this solution was then added 24.8 g. of hexaethylene glycol dichloride prepared from 33.0 g. hexaethyleneglycol, 18.5 g. pyridine and 27.8 g. thionyl chloride. The solution of sodium salt and glycol chloride was heated at 70°C. for 5 hours, at 100°C. for 4 hours and finally at 160°C. for 40 hours. A yield of 68.5 per cent was obtained.

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[73] British P. 393,619, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, **27**, 5975.

[74] K. H. Hoover, U. S. P. 1,934,309, Nov. 7, 1933, to American Soap and Glycerine Producers; *Brit. Chem. Abs.* **B**, 1934, 872; *Chem. Abs.*, 1934, **28**, 485.

[75] H. L. Cox and T. D. Roper, Jr., U. S. P. 2,044,468, June 16, 1936, to Union Carbide and Carbon Corp.; *Chem. Abs.*, 1936, **30**, 5237. French P. 796,156, 1936, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1936, **30**, 5590.

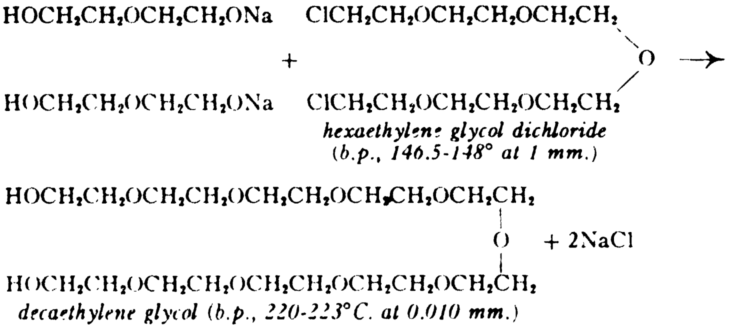
[76] T. Evans and K. R. Edlund, U. S. P. 1,968,033, July 31, 1934, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 5832; *Brit. Chem. Abs.* **B**, 1935, 715.

[77] H. L. Cox and T. F. Carruthers, U. S. P. 2,046,150, June 30, 1936, to Union Carbide and Carbon Corp.; *Chem. Abs.*, 1936, **30**, 5590. British P. 437,790, 1935, to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1936, 88; *Chem. Abs.*, 1936, **30**, 2200. *Cf.* also British P. 440,986, 1935; *Brit. Chem. Abs.* **B**, 1936, 263.

[78] E. F. Izard, U. S. P. 1,991,391, Feb. 19, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1936, 89; *Chem. Abs.*, 1935, **29**, 2176. See also, U. S. P. 2,006,555, July 2, 1935; *Brit. Chem. Abs.* **B**, 1936, 1141; *Chem. Abs.*, 1935, **29**, 5460.

[79] E. F. Izard, U. S. P. 2,008,716, July 23, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1936, 752; *Chem. Abs.*, 1935, **29**, 5949.

[80] S. Z. Perry and H. Hibbert, *Can. J. Research*, 1936, **14B**, 77; *Chem. Abs.*, 1936, **30**, 4150.



$$\begin{matrix} HOCH_2CH_2OCH_2CH_2ONa & ClCH_2CH_2OCH_2CH_2OCH_2CH_2 & \\ + & & \diagdown O \rightarrow \\ HOCH_2CH_2OCH_2CH_2ONa & ClCH_2CH_2OCH_2CH_2OCH_2CH_2 & \diagup \end{matrix}$$

hexaethylene glycol dichloride
(*b.p., 146.5-148° at 1 mm.*)

$$\begin{matrix} HOCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2 \\ | \\ O \quad + 2NaCl \\ | \\ HOCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_2 \end{matrix}$$

decaethylene glycol (b.p., 220-223°C. at 0.010 mm.)

The polyethylene glycols are solvents with low volatility and are miscible with water. They may be incorporated in a fatty acid soap for use with chloroform or carbon tetrachloride in dry-cleaning.[81] By heating diethylene glycol monoethyl ether to above 250°F. with boric acid and a base (such as ammonium, sodium or potassium hydroxide or an ethanolamine) a liquid is obtained which may be used as the electrolyte in an electrolytic condenser.[82] The polyglycerols (higher than 3 molecules) incorporated with 10 to 30 per cent water and a small proportion of a hygroscopic substance (other than the polyglycerols) are suggested as lubricants for valves and stopcocks.[83]

The derivatives of polyethylene glycol have been used in many ways. A large number of mixed esters and ethers including alkoxyacetates and alkyl and tetrahydrofurfuryl ethers have been advocated as solvents for refrigerants such as monofluorodichloromethane or methyl chloride.[84] Merrill[85] prepared the arsenites of polyglycols, or their monoethers, by heating with arsenious oxide at 135° to 145°C. until the calculated amount of water separated. An inorganic acid catalyst (hydrogen chloride) may be employed. The arsenites may be used in conjunction with petroleum fractions as insecticides and wood preservatives.

A series of compounds, designated "hydrophilic lipins" have been prepared by partial esterification of polyglycols or glycerols, followed by sulphating.[86] The esters, which contain fatty acid and sulphate groups, are reported to be applicable as softening, wetting, emulsifying, detergent, frothing and penetrating agents. One such compound, the ammonium salt of lauryl diethylene glycol sulphate was made by dissolving monolauryl diethylene glycol in chloroform, and treating with chlorosulphonic acid dissolved in the same solvent. When all the acid had been added, the resulting mixture was aspirated with a dry, inert gas to remove hydrogen chloride, and ammonia gas was incorporated to furnish the ammonium salt. Among the uses suggested for compounds of this general class are included the preparation of cake-batter ingredients,[87] confections,[88] and cosmetic creams.[89]

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[81] British P. 407,088, 1932, to Roessler and Hasslacher Chem. Co.; *Brit. Chem. Abs.* **B**, 1934, 412.

[82] F. C. Stephan, British P. 439,788, 1935, to The Telegraph Condenser Co. Ltd.; *Chem. Abs.*, 1936, **30**, 3336. *Cf.* British P. 448,830, 1936; *Chem. Abs.*, 1936, **30**, 8046. On the purifications of glycols and their ethers, see British P. 430,234, 1934; *Chem. Abs.*, 1935, **29**, 7346; *Brit. Chem. Abs.* **B**, 1935, 761.

[83] K. Noack, U. S. P. 2,015,867, Oct. 1, 1935; *Chem. Abs.*, 1935, **29**, 8321.

[84] G. F. Zellhoefer, U. S. P. 2,040,895; 2,040,896; 2,040,899; 2,040,900; 2,040,901; 2,040,904; 2,040,905; 2,040,906; 2,040,907; 2,040,908; 2,040,909; 2,040,910; 2,040,911; 2,040,912, May 19, 1936; *Chem. Abs.*, 1936, **30**, 4366.

[85] D. R. Merrill, U. S. P. 1,988,176, Jan. 15, 1935, to Union Oil Co. of Calif.; *Brit. Chem. Abs.* **B**, 1935, 1130; *Chem. Abs.*, 1935, **29**, 1573.

[86] B. R. Harris, U. S. P. 2,023,387 and 2,023,388, Dec. 3, 1935; *Chem. Abs.*, 1936, **30**, 1465, 733; *Brit. Chem. Abs.* **B**, 1936, 1192.

Diethylene glycol has been suggested as an hygroscopic substance for tobacco.[90] It is reported that cigarettes prepared from such tobacco are less irritating when smoked than those containing either glycerol or devoid of any moistening agent. Experiments, conducted on patients who were apparently affected by glycerol-containing cigarettes, showed that there was some difference in the behavior of the two hygroscopic agents from this standpoint.

The dinitrate of diethylene glycol may be prepared by adding (at 10° to 15°C.) the glycol to a mixture containing water, nitric and sulphuric acids. The product may be used to decrease the sensitivity of glyceryl trinitrate to shock.[91] Polyglycol nitrates may be recovered from the spent acid by washing with the nitrate of another polyhydric alcohol, e.g., nitroglycerol.[92]

The propionates of such polyhydric compounds as di- and tri-ethylene glycol, may be incorporated in compositions containing cellulose ethers or esters.[93] On the other hand the ethyl[94] and butyl[95] ethers of diethylene glycol have been employed in liquids intended for the transmission of pressure. For example, such a liquid medium may contain 50 per cent castor oil, 25 per cent triacetin, and 25 per cent diethyleneglycol monobutyl ether. It has been suggested that the butyl ether of diethylene glycol may be used in conjunction with *o*-dichlorobenzene for dewaxing oils.[96]

PROPENE AND HIGHER GLYCOLS

Glycols containing more than 2 carbon atoms, which include 1,2-, 1,3- and other diols, have attracted considerably less interest than ethylene glycol. Propene glycol may be prepared by saponification of propene dichloride. Klebanskii and Dolgopol'skii[97] have found that heating 1,2-dichloropropane with aqueous sodium carbonate at 209°C. and 48 atm. pressure gave a yield of only 48 per cent. Using sodium bicarbonate and carrying out the reaction at 210°C. and 182 atm. pressure raised the yield to 60 or 65 per cent and gave 7 to 8 per cent of unsaturated compounds. The 1,2-glycol which was formed in these reactions was estimated by oxidation with potassium dichromate:

$$3CH_3CH(OH)CH_2OH + 4K_2Cr_2O_7 + 16H_2SO_4 \longrightarrow 3CH_3COOH + 3CO_2 + 4K_2SO_4 + 4Cr_2(SO_4)_3 + 22H_2O$$

Bowden and Adkins[98] observed the formation of propane-1,2-diol on hydrogenation of butyl lactate in the presence of a copper chromite catalyst at 250°C. and 150 to

[87] B. R. Harris, U. S. P. 2,024,357, Dec 17, 1935; *Chem. Abs*, 1936, **30**, 1144 B. R Harris and M. C. Reynolds, U. S. P. 2,026,631, Jan. 7, 1936; *Brit Chem Abs.* B, 1937, 84; *Chem. Abs.*, 1936, **30**, 1143.

[88] B. R. Harris, U. S P. 2,024,985, and 2,024,986, Dec. 31, 1935; *Chem Abs*, 1936, **30**, 1144; *Brit. Chem. Abs.* B, 1936, 1233.

[89] B. R. Harris, U. S. P. 2,052,025 and 2,052,026, Aug. 25, 1936; *Chem Abs*, 1936, **30**, 6824.

[90] See C. F. Bailey and A. W. Petre. *Ind. Eng. Chem*, 1937, **29**, 11. G Mulinos and R. L. Osborne, *Proc. Soc. Exptl. Biol. Med*, 1934, **32**, 241; *Chem Abs*, 1935, **29**, 4824

[91] A. Hough, U. S. P. 1,936,020. Nov. 21, 1933; *Chem. Abs.*, 1934, **28**, 783; *Brit. Chem. Abs.* B, 1934, 824.

[92] German P. 592,007. 1934, Westfalisch Anhaltische Sprengstoff A G.; *Chem. Abs.*, 1934, **28**, 2730.

[93] H. S. Holt, U. S. P. 2,031,603, Feb. 25, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 2200.

[94] R. R. Fulton, U. S. P. 1,986,260, Jan. 1, 1935, to Puritan Soap Co.; *Brit. Chem. Abs.* B, 1935, 1027; *Chem. Abs.*, 1935, **29**, 1183.

[95] French P. 778,271, 1935, to Automotive Products Co., Ltd., *Chem. Abs.*, 1935, **29**, 4485.

[96] B. Y. McCarty and W. E. Skelton, U. S. P. 1,995,153, March 19, 1935, to Texas Co.; *Brit. Chem. Abs.* B, 1936, 260; *Chem. Abs.*, 1935, **29**, 3149.

[97] A. L. Klebanskii and I. M. Dolgopol'skii, *J Applied Chem. (U.S.S.R.)*, 1934, 7, 1181; *Chem. Abs.*, 1935, **29**, 5814; *Brit. Chem. Abs.* A, 1935, 325.

[98] E. Bowden and H. Adkins, *J.A.C.S.*, 1934, **56**, 689; *Chem. Abs.*, 1934, **28**, 2699; *Brit. Chem. Abs.* A, 1934, 521. See also, Carleton Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Company, New York, 1930.

200 atm. pressure. Another method of synthesis is hydrogenation of glycerol in the presence of a nickel-chromium oxide catalyst at 200°C. or higher and 2000 lbs. pressure.[99]

Schierholtz and Staples[100] have reported the physical properties of the propene and two of the butene glycols. 1,3-Butene glycol, since it could not be prepared from an olefin, was made in 75 per cent yield by the reduction of acetaldol with aluminum amalgam.

$$CH_3CH(OH)CH_2CHO + H_2 \longrightarrow CH_3CH(OH)CH_2CH_2OH$$

Some of the results obtained by Schierholtz and Staples are given in Table 118. The constants A and B for the vapor pressure equation:

$$\log_{10} p = B - \frac{A}{T}$$

which has been mentioned in connection with the properties of ethylene glycol are also given in the table.

TABLE 118.—*Physical Constants of Glycols.*

Glycol	B.P., °C.	Refractive Index n_D	at °C.	Density d_4	at °C.	Constants A	B	Range (°C.)	A	B	Range (°C.)
1,2—Propene	187.4°	1.43162	25	1.0354	23	3039.0	9.5157	80-130	2925.2	9.2317	130-187.5
1,3—Propene	214.7°	1.43847	25	1.0538	20	3305.4	9.6951	110-160	3154.9	9.3484	150-214.5
1,3—Butene	207.5°	1.44098	25	1.0053	20	3116.7	9.3890	100-150	3035.6	9.1979	150-207.5
2,3—Butene	182.5°	1.43637	25	1.0033	20	3023.9	9.5521	80-130	2907.1	9.2616	130-182.5

An interesting method for the synthesis of glycols by hydroxylation of olefinic bonds has been described by Milas and Sussman.[101] Employing *ter*-butyl alcohol these workers found that an anhydrous solution of hydrogen peroxide reacted with olefins in the presence of osmium tetroxide (dissolved in *ter*-butanol) to give glycols. For example, from 7 g. (0.1 mol.) of trimethylethylene (b.p. 38.3-38.4°C.), 48.4 cc. (0.1 mol.) of 7.03 per cent hydrogen peroxide reagent and 1 cc. of osmium tetroxide solution, reacted at room temperature for 24 hours, permitted the recovery of 2.9 g. of olefin and 2.3 g. (37.8 per cent yield) of a glycol. The product boiled at 175°C. and had a density of 0.992 at 25°. These values are in agreement with those given by Krassuski[102] (b.p. 176-8°, d_0^0 0.9893.) for the product which was prepared from trimethylethylene bromide and lead oxide. By their method, Milas and Sussman succeeded in synthesizing isobutene glycol, glycerol, phenyl-glyceric acid (from cinnamic acid), dihydroxybutyric acid (from crotonic acid), and *meso*- and *dl*-tartaric acids from maleic and fumaric acids, respectively.

The formation of butanediol-2,3 by fermentation of sucrose by *Aerobacter* has been studied by Kendall.[103] He found that yields corresponding to 50 per cent of the weight of sucrose used could be obtained by employing a medium containing 8 per cent sucrose, 0.175 per cent magnesium sulphate, 0.3 per cent or more of ammonium chloride, 0.175 per cent of disodium phosphate and a trace of calcium chloride. The optimum *p*H was 6.2.

Both *dl*-2,3-butanediol and *meso*-2,3-butanediol have been prepared by Wilson and Lucas.[103a] Their method comprised treatment of butene-2 with hypochlorous acid to secure the corresponding chlorohydrin, subjecting this to the action of potassium hydroxide to obtain the alkene oxide, and hydrating the latter with dilute aqueous perchloric acid. *cis*-Butene furnished the *dl*-compound and *trans*-butene the *meso*-derivative. Some of the physical properties of these two optically inactive glycols are given in Table 118A.

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[99] A. W. Larchar, U. S. P. 1,963,997, June 26, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 5077; *Brit. Chem. Abs.* **B**, 1935, 396.

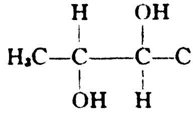
[100] O. J. Schierholtz and M. L. Staples, *J.A.C.S.*, 1935, **57**, 2709, *Chem. Abs.*, 1936, **30**, 1624; *Brit. Chem. Abs.* **A**, 1936, 279.

[101] N. A. Milas and S. Sussman, *J.A.C.S.*, 1936, **58**, 1302; *Chem. Abs.*, 1936, **30**, 5946.

[102] K. Krassuski, *J. Russ. Phys. Chem. Soc.*, 1902, **33**, 791; *Chem. Zentr.*, 1902, **1**, 628.

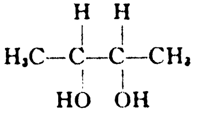
[103] A. R. Kendall, *Iowa State Coll. J. Sci.*, 1934, **9**, 171; *Chem. Abs.*, 1935, **29**, 5217. See also, J. Stastny, *Vestnik Ceskoslov. Akad. Zemedelske*, 1932, **8**, 6871; *Chem. Abzor. 8 Abstract Sect.*, 187; *Chem. Abs.*, 1934, **28**, 3831. H. Moureu and M. Dode, *Bull. assoc. chim. sucr. dist.*, 1934, **51**, 247; *Chem. Abs.*, 1934, **28**, 6239.

[103a] C. E. Wilson and H. J. Lucas, *J.A.C.S.*, 1936, **58**, 2397; *Chem. Abs.*, 1937, **31**, 657.



$$H_3C-\underset{OH}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-CH_3$$

dl-2,3-butanediol



$$H_3C-\underset{HO}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-CH_3$$

meso-2,3-butanediol

TABLE 118A.—*Some Physical Properties of Inactive 2,3-Butanediols.*

Glycol Configuration	*meso*	*dl*
Melting point	34.4°C.	7.6°C.
Boiling point (742 mm.)	181.7°C.	176.7°C.
Boiling point (16 mm.)	89°C.	86°C.

Flavitzkii[104] has shown that the glycol prepared from amylene (obtained from amyl alcohol of fermentation) has the structure of isopropyl ethylene glycol. This was indicated by the formation of isobutyric acid on oxidation with sulphuric acid and potassium dichromate. According to Wiemann[105] oxidation of diprop-1-enyl ethylene glycol (4,5-dihydroxyoctadiene-2,6) results in the formation of a dimethyl hexitol (hexahydroxyoctane, m.p. 161-2°C.). Glycols are also said to be formed by the oxidation in acetic, propionic or butyric acid solution of olefins of 8 or more carbon atoms by hydrogen peroxide.[106] This result is in keeping with that reported by Milas and Sussman, mentioned previously in this chapter. For example, a 94 per cent yield of hexadecane-1,2-diol is said to be obtained from 224 g. of hexadecene-1 in solution in 100 g. acetic acid at 95°C. by oxidation with 170 cc. of 30 per cent hydrogen peroxide.

Edlund[107] has described the preparation of glycol ethers (which can be used as solvents) by reaction with an alcohol of an olefin oxide containing 4 or more carbon atoms. In this way 2-methoxy- and 2-ethoxy-1,1-dimethyl-ethanol (b.p. 142° and 147.8°C., respectively) were made from isobutene oxide and methanol or ethanol.

Reactions of the glycols of 3 or more carbon atoms parallel those of ethylene glycol. There is, for example, the possibility of forming esters and ethers, and of oxidation to carbonyl groups and finally complete oxidation of the molecule.[108] For example, oxidation of polyhydric alcohols to the corresponding carbonyl compounds may be brought about by the action of 1 mole of available oxygen on 2 carbinol groups in the presence of an activated copper catalyst at 270°C. In this way, biacetyl may be prepared from 2,3-butene glycol.[109]

Diols may be dehydrated at temperatures below their boiling point by the action of oxides of aluminum, zirconium or thorium.[110] For example, 1,12-octadecanediol may be converted into octadecenol by this procedure.

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[104] F. Flavitzkii, *Ber.*, 1877, **10**, 230; *J.C.S.*, 1877, **32**, 286.

[105] J. Wiemann, *Compt. rend.*, 1935, **200**, 2021; *Chem. Abs.*, 1935, **29**, 5816; *Brit. Chem. Abs.* **A**, 1935, 1104.

[106] British P. 449,060, 1935, to Böhme Fettchemie-Ges.m.b.H.; *Chem. Abs.*, 1936, **30**, 7587; *Brit. Chem. Abs.* **B**, 1936, 823. British P. 449,221, 1936; French P. 795,391, 795,392, 1936; *Chem. Abs.*, 1936, **30**, 5238.

[107] K. R. Edlund, U. S. P. 1,968,032, July 31, 1934, to Shell Development Co.; *Brit. Chem. Abs* **B**, 1935, 618; *Chem. Abs.*, 1934, **28**, 5832.

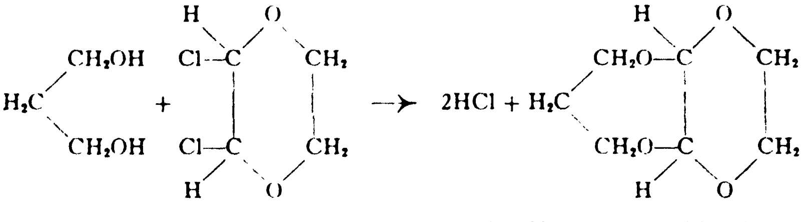
[108] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. Also this chapter under properties of ethylene glycol.

[109] S. H. McAllister and M. de Simo, U. S. P. 2,051,266, Aug. 18, 1936, to Shell Development Co., *Chem. Abs.*, 1936, **30**, 6763.

[110] British P. 413,909, 1934, to H. Th. Böhme, A.-G.; *J. Inst. Pet. Tech.*, 1934, **20**, 541A; *Chem. Abs.*, 1935, **29**, 176; *Brit. Chem. Abs.* **B**, 1934, 824. French P. 762,001; *Chem. Abs.*, 1934, **28**, 5077.

Lepkovsky and co-workers[111] have shown further that fatty acid esters of ethylene and diethylene glycol were toxic and caused enlargements and lesions in the kidneys of rats. On the other hand, the corresponding esters of propene glycol were nontoxic and produced good growth.

A rather interesting reaction of trimethylene glycol is that with 2,3-dichloro-1,4-dioxane which results in the formation of a cyclic ether:



Interaction occurs when the reactants are heated for 20 hours in boiling benzene.[112] The product is a mixture of two solid stereoisomers.

The action of *Aspergillus niger* (a mold) on propane-, butane-, pentane-, and hexane-1,2-diols has been investigated by Walti.[113] He showed that oxidation of the secondary alcohol group took place with the formation of a 1-hydroxyalkanone-2 except in the case of the hexanediol, which was unaffected. The products were optically active as were the unreacted glycols which were recovered.

The uses of 1,2- and 1,3-propene glycol parallel in some measure those of diethylene and ethylene glycol. For example, they have been used in amounts of 16 per cent of the water content of the product as preservatives for egg material when the latter is utilized in cosmetics.[113a] Trimethyleneglycol diacetate and various ethers and esters of the glycol have also been suggested as solvents for fluorodichloromethane when the latter is used as a refrigerant.[114]

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[111] S. Lepkovsky, R. A. Ouer and H. M. Evans, *J. Biol. Chem.*, 1935, **108**, 431; *Chem. Abs.*, 1935, **29**, 4416. L. I. Howe and R. F. Ruttan, *Can. Chem. J.*, 1918, **2**, 196; *Chem. Abs.*, 1918, **12**, 2545

[112] J. Böeseken, F. Tellegen and P. Maltha, *Rec. trav. chim.*, 1933, **52**, 1067; *Chem. Abs.*, 1934, **28**, 4423

[113] A. Walti, *J.A.C.S.*, 1934, **56**, 2723; *Chem. Abs.*, 1935, **29**, 731; *Brit. Chem. Abs.* **A**, 1935, 193

[113a] W. Kritchevsky, B. R. Harris and C. J. Beckert, U. S. P. 1,924,947, Aug. 29, 1933; *Chem. Abs.*, 1933, **27**, 5484; *Brit. Chem. Abs.* **B**, 1934, 556.

[114] G. F. Zellhoefer, U. S. P. 2,040,897; 2,040,901, May 19, 1936; *Chem. Abs.*, 1936, **30**, 4366.

Chapter 23

Production, Properties and Uses of Olefin Oxides and Their Derivatives

Of a variety of methods for the preparation of olefin oxides, the main ones fall into two groups:[1]

1. The action of alkalies, such as sodium hydroxide, on α-alkene halohydrins, by which the elements of hydrogen halide are removed.
2. The direct oxidation of olefins, reaction being carried out in the presence of a catalyst.

Insofar as known, large-scale operations involve only the first procedure, i.e., heating alkene chlorohydrins with alkalies, although there is considerable interest in the oxidation procedure. While it is doubtful if the latter method is being intensively employed technically at the present time, it is apparent that the trend is now definitely in that direction.

PRODUCTION OF OLEFIN OXIDES FROM CHLOROHYDRINS

Thole, Birch and Scott[2] recommend that a solution of ethylene chlorohydrin be added to somewhat more than the theoretical requirement of alkali (sodium hydroxide solution) at 10 to 20°C. The mixture is then allowed to react in a packed column at 35 to 50°C. under reduced pressure (90-105 mm.). Ethylene oxide is rapidly liberated and collected in a separate vessel as solid hydrate. A much shorter period of heating at higher temperatures is employed by Britton, Nutting and Petrie.[3] They suggest that substantially equimolecular proportions of alkene chlorohydrin and alkali hydroxide, carbonate or bicarbonate be heated under slightly superatmospheric pressure for a very short time. The period required is usually 5 to 60 seconds at temperatures between 90° and 150°C. By cooling rapidly to below 70°C. and distilling off the olefin oxide the formation of by-products is avoided. The method may be readily operated as a continuous process. Another procedure consists in passing vapor of the chlorohydrin, such as ethylene chlorohydrin or menthol chloride, over an active catalyst such as magnesium oxide, copper oxide, or a salt of either magnesium or copper.[4] The contact agent is more effective if mounted on a carrier.

Other chlorinated compounds besides the chlorohydrins have been found to yield ethylene oxide on treatment with alkalies. An example is β-chloroethyl acetate, which is said to give good results if sodium hydroxide is slowly added to it with constant stirring. The temperature of the mixture should be kept between the limits 40° and 150°C.[5]

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[1] For a review of these, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

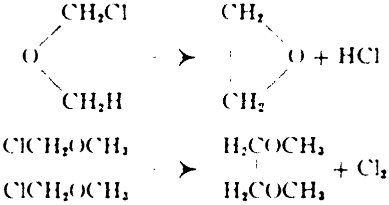
[2] F. B. Thole, S. F. Birch and W. D. Scott, U. S. P. 1,986,082, Jan. 1, 1935, to Anglo-Persian Oil Co., Ltd.; *Chem. Abs.*, 1935, **29**, 1103. British P. 374,864, 1932; *Chem. Abs.*, 1933, **27**, 3952; *Brit. Chem. Abs.* **B**, 1933, 878.

[3] E. C. Britton, H. S. Nutting and P. S. Petrie, U. S. P. 1,996,638, April 2, 1935, to Dow Chemical Co.; *Chem. Abs.*, 1935, **29**, 3350; *Brit. Chem. Abs.* **B**, 1936, 310.

[4] W. Schoeller, E. Schwenk, E. Borgwardt and F. Aichner, U. S. P. 1,967,433, July 24, 1934, to Schering-Kahlbaum A.-G.; *Chem. Abs.*, 1934, **28**, 5832. French P. 728,849, 1931; *Chem. Abs.*, 1932, **26**, 5963.

Dominik and Bartkiewiczówna[6] added an aqueous solution of ethyl hypochlorite drop-wise to calcium oxide or sodium hydroxide in a flask heated in an oil bath. A manometer was connected with a reflux condenser, and from the observed rise in pressure during the experiment, the yield of ethylene oxide was calculated. Better results were obtained with calcium oxide than with aqueous sodium hydroxide. The yield of ethylene oxide in the former case was as high as 90 per cent of the theoretical amount.

Another method,[7] applicable also for the preparation of cyclic and open chain ethers, consists in heating halogenated dialkyl ethers with finely divided metals. Copper, nickel and platinum have been found effective. Reactions in the liquid phase are carried out under 200 atmospheres pressure at temperatures between 50° and 100°C. Vapor-phase changes take place at temperatures from 100 to 250°C. When monochlorodimethyl ether is heated at 100°C. with metallic sodium, ethylene oxide is produced by removal of hydrogen chloride from one molecule of the chloro-compound. However, if two molecules of the ether are involved, only halogen is split off, and by condensation the dimethyl ether of ethylene glycol is formed.



Similarly, ethylene oxide and dioxane result from dichlorodiethyl ether using copper at 150°C. and 150 atmospheres pressure.

Olefin Oxides by Oxidation of Unsaturated Hydrocarbons

Francon[8] has reported a series of experiments on the preparation of ethylene oxide by direct oxidation of ethylene in the presence of an activated catalyst. The raw material, a gas mixture containing 92 per cent of ethylene, was produced by catalytic dehydration of ethanol. The results of Francon's tests are summarized as follows:

The optimum working temperature was found to be 375°C. and the most effective air-ethylene ratio was 10:1. Carbon dioxide was formed simultaneously with the oxide, but if water was introduced into the reaction mixture smaller yields of both products resulted, the oxide being affected less than carbon dioxide. The optimum gas flow, with a tube of 23 mm. internal diameter, was 80 liters per hour. At this rate, varying the proportions of air and ethylene reduced the formation of ethylene oxide and (to a less extent) increased that of carbon dioxide. At temperatures below 375°C. the production of ethylene oxide was lowered considerably, with practically no change in carbon dioxide yield. Above 375°C., however, both oxide and dioxide increased, the latter more than the former. Raising the pressure to 50 kg. per sq. cm. caused the development of more carbon dioxide at the expense of ethylene oxide, possibly because of partial combustion of the latter. Under optimum conditions, the production of carbon dioxide was attributed to direct oxidation of the ethylene gas.

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[5] E. C. Britton, G. H. Coleman and B. Mate, U. S. P. 2,022,182, Nov. 26, 1935, to Dow Chemical Co.; *Chem. Abs.*, 1936, **30**, 737; *Brit. Chem. Abs.* **B**, 1936, 1192.

[6] W. Dominik and J. Bartkiewiczówna, *Przemysl Chem.*, 1934, **18**, 373; *Chem. Abs.*, 1935, **29**, 5815; *Brit. Chem. Abs.* **A**, 1935, 194.

[7] British P. 435,110, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 1387; *Brit. Chem. Abs.* **B**, 1935, 1037.

[8] J. Francon, *Chim. et ind.*, 1933, **29**, (June Spec. No.), 869; *Chem. Abs.*, 1934, **28**, 465; *Brit. Chem. Abs.* **B**, 1933, 953.

According to Francon, industrial coke-oven gas may be used in this process if impurities, such as acetylene and compounds of sulphur and phosphorus, have been removed. These catalyst poisons may be eliminated by leading the raw gases through a purifier containing copper oxide maintained at temperatures of 150° to 200°C. For work on the commercial scale with treated coke-oven gases, an air-ethylene ratio of 1:3 is suggested, with a further supplement of about 5 per cent of pure oxygen. The gaseous mixture could then be conducted through a number of catalyst tubes in which the activity of the contact mass increased in the successive stages. Unchanged ethylene might be recycled, or hydrated to give ethyl alcohol.

Later, Francon[9] described the catalyst employed in his method. It was composed of silver or gold, or a mixture of the two, either as metals or as alloys containing small percentages of a third metal, such as copper or iron. It may be used in the form of fragments, thin sheets or flakes. An example is fine leaflets of silver containing a small amount of copper and gold.[10] These were made by rolling the alloy to form a foil, shredding the latter in a liquid medium, and finally drying and screening the metallic particles.

Admixtures of hydrogen, carbon dioxide and steam are permissible with the ethylene-oxygen reactants when the reaction temperature ranges from 150° to 400°C.

In a similar process for ethylene oxidation[11] the addition of water to the reaction mixture is said to minimize the formation of by-products, such as aldehydes. The catalysts recommended for this treatment are the metals antimony, lead, bismuth, silver, arsenic, nickel, tin, gold, copper, or iron. They may be used alone or as mixtures, or in admixture with their oxides. Hydrogen up to 5 per cent of the total volume of gases may be admitted. Temperatures between 150 and 400°C. and pressures up to 50 atmospheres may be employed. A typical reaction vessel consists of a silica tube containing a silver catalyst, or silver powder mounted on a carrier.

Several modifications of the above procedure have been disclosed. In one of these,[12] carbon dioxide is suggested as an alternative inert diluent, and pressures below atmospheric are recommended. The catalyst consists of silver activated by small amounts of either gold, copper or iron. As before, the reaction takes place at 150° to 400°C. in the presence of water. Another method[13] proposed by the same workers suggests employment of large proportions of carbon dioxide or nitrogen as diluent (at least 50 per cent by volume), and requires the complete absence of water. High temperatures, 300° to 400°C., and pressures up to 50 atmospheres, are employed. Contact agents consist of metallic silver, or silver containing small quantities of gold or copper.

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[9] J. Francon, French P. 794,751, 1936; *Chem. Abs.*, 1936, **30**, 5235. See also British P. 444,186, 1936, to Soc. francaise de catalyse généralisée; *Brit. Chem. Abs.* B, 1936, 487; *J. Inst. Pet. Tech.*, 1936, **22**, 272A; *Chem. Abs.*, 1936, **30**, 5588.

[10] French P. 45,609, 1935, addition to 739,562, to Soc. francaise de catalyse généralisée; *Chem. Abs.*, 1936, **30**, 3837.

[11] British P. 402,438, 1933, to Soc. francaise de catalyse généralisée; *Chem. Abs.*, 1934, **28**, 2731; *Brit. Chem. Abs.* B, 1934, 232; *J. Inst. Pet. Tech.*, 1934, **20**, 192A. French P. 739,562, 1933; *Chem. Abs.*, 1933, **27**, 2163.

[12] British P. 402,749, 1933, addition to 402,438, to Soc. francaise de catalyse généralisée; *Brit. Chem. Abs.* B, 1934, 266; *J. Inst. Pet. Tech.*, 1934, **20**, 115A; *Chem. Abs.*, 1934, **28**, 2731. French P. 41,811, 1933; *Chem. Abs.*, 1933, **27**, 4546.

[13] British P. 431,966, 1935, to Soc. francaise de catalyse généralisée; *Chem. Abs.*, 1936, **30**, 112; *Brit. Chem. Abs.* B, 1935, 839; *J. Inst. Pet. Tech.*, 1935, **21**, 383A. French P. 771,650, 1934; *Chem. Abs.*, 1935, **29**, 819. T. E. Lefort, U. S. P. 1,998,878, Apr. 23, 1935; *Chem. Abs.*, 1935, **29**, 4029.

Silver is the metal most generally recommended in the preparation of ethylene oxide from ethylene. It may be used in the form of wire, foil, or powder, or in colloidal suspension, either alone or with various metallic promoters. An active contact mass may be made by the decomposition of certain organic salts of silver, in particular the oxalate, by heating at 300°C.[14] As activators, the following metals are reported to be efficient: copper, gold, iron, manganese, cobalt, nickel, cerium, thorium and zinc. The most effective temperatures are said to be from 350° to 400°C. The gas mixture may carry steam, nitrogen or other diluent, and should contain 8 to 9 per cent by volume of ethylene.

The use of certain metallic compounds as catalysts for the oxidation of olefins to the corresponding oxides is advocated by Dreyfus.[15] The substances suggested are oxides of selenium, copper, silver, mercury, zinc, lead, antimony, arsenic and tellurium. Optimum conditions of temperature and pressure are given at 200° to 500°C. and above 10 atmospheres, respectively.

OLEFIN OXIDATIONS WITHOUT CATALYSTS

At high temperatures and in the absence of catalysts, the chief products of the oxidation of olefins are aldehydes and acids. For effecting the treatment in gaseous phase when it is desired to produce olefin oxides or glycols, temperatures from 250-600°C. are used.[16] The reaction vessel should be free from packing and have a surface-volume ratio of not over 4:1. The conversion period is longer than 10 seconds at 250-350°C. but only about 1 second at 450-600°C. Yields obtained in two instances were as follows: A 4:1 mixture of ethylene and oxygen, heated for 25 seconds at 315°C., gave 11.8 per cent ethylene oxide, 34.7 per cent formaldehyde and 6.9 per cent formic acid, the results being based on the amount of ethylene decomposed. A similar mixture of propene and oxygen held for 28 seconds at 270-360°C. produced propene oxide, propene glycol, propionaldehyde, propionic acid, acetic acid, formic acid, acetaldehyde and formaldehyde.

ETHYLENE OXIDE BY HYDROLYSIS OF ESTERS

Alkene oxides are formed by hydrolysis of volatile fatty esters having a double bond and a carboxyl group attached to the same carbon atom.[17] Ammonia or an organic base may be used to effect the reaction. For instance, a mixture of 5 parts of vinyl acetate, $CH_2{=}CHCO_2CH_3$, with 5 parts of pyridine and 1 part of water is heated to 100°C. in a vessel connected with a reflux condenser, the temperature of which is maintained at 20°C. Or, vapors of the vinyl ester (5 parts) and ammonia (1 part) may be passed through a silica-packed tube at 245-250°C. In either case, ethylene oxide is formed and may be separated by fractional distillation, the unchanged ester being first condensed by cooling to 20°C. and the oxide liquefied by further cooling.

BEHAVIOR OF ETHYLENE OXIDE

Properties of Ethylene Oxide. Ethylene oxide is a colorless, volatile liquid of $d_4^{?}$ 0.887. The pure substance boils at 10.7°C. It has a sweetish odor and mixes with water in all proportions. Its vapor forms explosive mixtures with air within very wide limits. The formation of binary mixtures as well as the boiling points of ethylene oxide-water or -alcohol admixtures were investigated by Kireev and Popov.[18]

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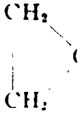
[14] British P. 434,011, 1935, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 737; *Brit. Chem. Abs.* **B**, 1935, 938; *J. Inst. Pet. Tech.*, 1935, **21**, 424A. French P. 788,975, 1935; *Chem. Abs.*, 1936, **30**, 1808. See also, A. J. van Peski, U. S. P. 2,040,782, May 12, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 4510.

[15] H. Dreyfus, French P. 770,420, 1934; *Chem. Abs.*, 1935, **29**, 474.

[16] British P. 400,297, 1932, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1934, 10.

[17] H. Dreyfus, British P. 449,875, 1936; *Brit. Chem. Abs.* **B**, 1936, 971; *Chem. Abs.*, 1936, **30**, 8242.

Very little work appears to have been done on the physical properties of ethylene oxide, attention having been directed more to its physiological and chemical reactions. The valence angle of the oxygen in  is somewhat smaller than the corresponding figure for dimethyl ether, which has no bond connecting the two carbon atoms. The values, calculated from Raman frequencies, are 64° and 102°, respectively.[19]

Storage and Shipment. A method intended to minimize deterioration of ethylene oxide during storage and shipment has been recommended by Cox and Greer.[20] It consists in contacting the organic substance with cuprous oxide, manganese dioxide, alloys of iron, nickel and chromium, or metallic copper, aluminum, chromium, nickel, zinc or cadmium. The same treatment may be applied for the preservation of other alkene oxides, as well as dialkene oxides, aliphatic ethers with more than four carbon atoms per molecule, substituted derivatives of aliphatic ethers, alkoxy alcohols and their derivatives.

Thermal Decomposition of Ethylene Oxide. Travers[21] has made a study of the changes which take place during the thermal decomposition of ethylene oxide. He maintains that neither the mechanism nor the rate of the reactions involved can be satisfactorily followed by measuring the rate of the increase in pressure at constant volume. He considers that the reactions depend on the surface of the system and involve a chain mechanism. On the other hand, Thompson and Meissner,[22] summarizing measurements of the rate of decomposition of ethylene oxide over the range 435-505°C., find their results to agree, in general, with those of Heckert and Mack.[23] The latter workers decided that the thermal decomposition of gaseous ethylene oxide in a Pyrex container at 380-444°C. is a strictly homogeneous gas reaction, occurring in two steps with probably acetaldehyde formation as an intermediate step. There seemed to be an induction period. A decrease in the velocity of decomposition on the addition of inert gases was proportional to the pressure ratio of inert gas to ethylene oxide. The depressants included argon and neon (least effective), carbon dioxide, carbon monoxide, nitrogen, methane, ethane, propane, isobutane, helium. Hydrogen, on the other hand, increased the velocity of decomposition. However, Thompson and Meissner were unable to detect acetaldehyde among the products at any stage of the decomposition over the temperature range studied. The chief yields were carbon monoxide and methane with some formation of hydrogen and ethane. These workers found the velocity constant to vary with pressure over the range 15-800 mm. At 475°C. the period of half change was almost independent of initial pressure at above 250 mm. Between 250 and 40 mm. there was a bimolecular relation between the half change period and initial pressure and another such region below 40 mm. With initial pressures over 300 mm. the energy of activation was found to be about 54,000 cal. and at about 20 mm. approximately 50,000 cal.

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[18] V. A. Kireev and A. A. Popov, *J. Applied Chem. (U.S.S.R.)*, 1934, 7, 489; *Chem. Abs.*, 1935, **29**, 2061; *Brit. Chem. Abs.* **A**, 1934, 1101.

[19] N. G. Pai, *Current Sci.*, 1934, **2**, 386; *Chem. Abs.*, 1934, **28**, 4175; *Brit. Chem. Abs.* **A**, 1934, 830.

[20] H. L. Cox and P. S. Greer, Canadian P. 348,473, 1935, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, **29**, 3150.

[21] M. W. Travers, *Nature*, 1935, **136**, 909; *Chem. Abs.*, 1936, **30**, 1642; *Brit. Chem. Abs.* **A**, 1936, 191. See also M. W. Travers and T. J. P. Pearce, *J. S. C. I.*, 1934, **53**, 321T; *Chem. Abs.*, 1935, **29**, 1057; *Brit. Chem. Abs.* **A**, 1935, 40. C. N. Hinshelwood, C. J. M. Fletcher, F. H. Verhoek and C. A. Winkler, *Proc. Roy. Soc. (London)*, 1934, **A146**, 327; *Brit. Chem. Abs.* **A**, 1934, 1311; *Chem. Abs.*, 1934, **28**, 7120.

[22] H. W. Thompson and M. Meissner, *Nature*, 1936, **137**, 870; *Brit. Chem. Abs.* **A**, 1936, 820; *Chem. Abs.*, 1936, **30**, 5488. *Trans. Faraday Soc.*, 1936, **32**, 1451; *Chem. Abs.*, 1936, **30**, 7988; *Brit. Chem. Abs.* **A**, 1936, 1208.

[23] W. W. Heckert and E. Mack, Jr., *J. A. C. S.*, 1929, **51**, 2706; *Chem. Abs.*, 1929, **23**, 5401; *Brit. Chem. Abs.* **A**, 1929, 1243.

Sickman[24] also reports that an induction period is exhibited in the pyrolysis of ethylene oxide and that the reaction is inhibited by the presence of inert gases. His results are in qualitative agreement with those of Heckert and Mack.[25] In a discussion of the various peculiarities of the ethylene-oxide pyrolysis, Fletcher[26] suggests the formation of free radicals and aldehydes at 400°C., followed by breaking up of the aldehydes, as an explanatory mechanism of the changes taking place. Fletcher found that at 443°C. acetaldehyde (exerting a pressure of 184 mm.) is half decomposed in 3 minutes in the presence of its isomer, ethylene oxide (partial pressure 17 mm.), whereas approximately 350 minutes were required with no ethylene oxide present. Later work by Travers and Seddon[27] points out the complexity of the changes involved in the thermal decomposition under consideration, in the case of both ethylene oxide and its isomer acetaldehyde. They found the latter, over a wide range of concentrations, to decompose mainly into methane and carbon dioxide at 360-500°C. in unpacked tubes, but into propene and carbon monoxide in packed tubes. However, some propene always appeared in the first case and underwent condensation producing 6-carbon and more complex hydrocarbons.

Echols and Pease[28] report confirmation of the observations of Heckert and Mack as to the cracking of *n*-butane, isobutane and propane in the presence of decomposing ethylene oxide at temperatures at which the normal decomposition of these paraffins is negligible. At a total pressure of about 500 mm. and a temperature of 425°C., the results given in Table 119 were obtained.

TABLE 119.—*Pyrolysis of Paraffins Admixed with Ethylene Oxide*

Hydrocarbon	Initial Ratio of Hydrocarbon to Ethylene Oxide	Ratio of Total Olefins to Carbon Monoxide
Ethane	1.6	<0.05
Propane	1.6	.55
Isobutane	1.7	.75
	1.6	1.2
n-Butane	4.1	4.5
	8.0	12.0

Echols and Pease point out the increase in the relative amount of olefin with the complexity of the paraffin and, in the case of *n*-butane, with the relative amount of the latter originally present. They report the rate of pressure increase as falling off rapidly on continued reaction, suggesting that products of paraffin decomposition are inhibiting reactivity. The effect of increases in temperature on the olefin-carbon monoxide ratio was not great. Other experiments were found to confirm the accelerated decomposition of acetaldehyde in the presence of ethylene oxide as reported by Fletcher and noted above.

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[24] D. V. Sickman, *J. Chem Physics*, 1936, **4**, 297; *Chem. Abs.*, 1936, **30**, 4077; *Brit. Chem. Abs.* **A**, 1936, 802.

[25] W. W. Heckert and E. Mack, Jr., *loc. cit.*

[26] C. J. M. Fletcher, *J.A.C.S.*, 1936, **58**, 534; *Chem. Abs.*, 1936, **30**, 2922; *Brit. Chem. Abs.* **A**, 1936, 570. C. J. M. Fletcher and G. K. Rollefson, *J.A.C.S.*, 1936, **58**, 2135; *Chem. Abs.*, 1937, **31**, 936.

[27] M. W. Travers and R. V. Seddon, *Nature* 1936, **137**, 906; *Chem. Abs.*, 1936, **30**, 5861; *Brit. Chem. Abs.* **A**, 1936, 825. R. V. Seddon and M. W. Travers, *Proc. Roy. Soc.* (*London*), 1936, **156A**, 234; *Chem. Abs.*, 1936, **30**, 7980.

[28] L. S. Echols, Jr., and R. N. Pease, *J.A.C.S.*, 1936, **58**, 1317; *Chem. Abs.*, 1936, **30**, 5933.

Toxicity of Ethylene Oxide. Ethylene oxide is known to possess the properties of an efficient insecticide and fumigant. The toxicological activity of the compound has been investigated with reference to possible hazards involved in the handling of the material industrially.

Waite, Patty and Yant[29] tested the physiological effects of ethylene oxide on small animals. It was concluded that the toxic effects of ethylene oxide vapor are comparable with those of ammonia, being less dangerous than sulphur dioxide and hydrogen chloride, but more harmful than chloroform or carbon tetrachloride. In view of its distinct lachrymatory properties, at comparatively safe dilutions, however, this material may be said to give ample warning of its presence in the atmosphere before any serious harm can be done.

When used as a fumigant, ethylene oxide is frequently mixed with carbon dioxide, which increases its insecticidal value while decreasing its inflammability. A review of the work on the toxicity of ethylene oxide-carbon dioxide mixtures has been presented by Popov, Bezzub and Lebedeva.[30] The effect of added carbon dioxide gas on the toxic action of ethylene oxide is highest at the ratio of 1:10 to 1:15. The ignition safety limit of such mixtures is at 1:7.5 volumes. Aetox gas, an industrial product[31] containing ethylene oxide and carbon dioxide, is reported to be nearly ten times as toxic as the oxide alone. It cannot be used in the fumigation of wheat grain because of its destructive action on germinative power.

The effect of the vapor of ethylene oxide on insects has been studied by Hase.[32] A concentration of 60 g. per cubic meter was found to destroy insect eggs in 24 hours.[33] Horsfall[34] has described the action of ethylene oxide on the bean weevil and the flour beetle.

Determination of Ethylene Oxide. The use of ethylene oxide in the fumigation of foodstuffs has necessitated its accurate determination in air and gases as well as in the stored materials. A most useful method, which can be adapted for the analysis of both liquids and gases containing ethylene oxide, is that first suggested by Deckert[35] and later modified by Lubatti.[36] It consists essentially in allowing the oxide to react with a known amount of standard hydrochloric acid solution. Ethylene chlorohydrin is formed, and the excess acid is titrated. The absorbent liquid must contain a high concentration of halogen ions. Lubatti recommends a saturated solution of magnesium chloride, which he reports gives results which approach the theoretical much more closely than those obtained when sodium chloride is employed for this purpose. The equivalent of at least 300 g. of chlorine per liter of solution must be present, but in any case the best result obtainable corresponds to only about 94 per cent of the theoretical amount of ethylene oxide. Waite, Patty and Yant[37] used 2*N* hydrochloric acid and avoided hydrolysis of the ethylene chlorohydrin formed by titrating the excess acid against standard barium hydroxide solution. Lubatti, as well as Waite and his co-workers, employed methyl orange as indicator.

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[29] C. P. Waite, F. A. Patty and W. P. Yant, *Pub. Health Rep.*, 1930, **45** (32), 1832; *Chem. Abs.*, 1930, **24**, 4849.

[30] P. V. Popov, K. E. Bezzub and N. I. Lebedeva, *Trans. Sci. Inst. Fertilisers and Insectofungicides* (*U.S.S.R.*), 1935, **123**, 264; *Chem. Abs.*, 1936, **30**, 3575. For the determination of ethylene oxide in fumigants see W. B. Brown, *J.S.C.I.*, 1936, **55**, 321T; *Chem. Abs.*, 1937, **31**, 974; *Brit. Chem. Abs.* **B**, 1936, 1191.

[31] Other trade-names for commercial mixtures of ethylene oxide and carbon dioxide are Carboxide and T-gas.

[32] A. Hase, *Z. Parasitenk.*, 1932, **4**, 369; *Brit. Chem. Abs.* **B**, 1932, 318. *Naturwissenschaften*, 1932, **20**, 345; *Chem. Abs.*, 1932, **26**, 4883.

[33] A. Hase, *Arb. biol. Reichsanst. Land- u. Forstwirt. Berlin-Dahlem*, 1932, **20**, 101; *Chem. Abs.*, 1934, **28**, 3192; *Brit. Chem. Abs.* **B**, 1933, 935; *Chem. Zentr.*, 1933, 1, 1991.

[34] W. R. Horsfall, *J. Econ. Entomol.*, 1934, **27**, 405; *Chem. Abs.*, 1934, **28**, 5588; *Brit. Chem. Abs.* **B**, 1934, 979.

[35] W. Deckert, *Z. anal. Chem.*, 1930, **82**, 297; *Chem. Abs.*, 1931, **25**, 263; *Brit. Chem. Abs.* **B**, 1931, 180.

[36] O. F. Lubatti, *J.S.C.I.*, 1932, **51**, 361T; *Chem. Abs.*, 1933, **27**, 245; *Brit. Chem. Abs.* **B**, 1933, 94.

[37] C. P. Waite, F. A. Patty and W. P. Yant, *loc. cit.*

A micromethod of analysis of ethylene oxide-containing gases has been developed by Lubatti[38] and may be used in conjunction with the Page sampling apparatus.[39] The absorbent liquid consists of a solution of 490 to 540 g. of magnesium bromide per liter in 0.025 to 0.1*N* sulphuric acid. Such a solvent is said to allow 100 per cent recovery of ethylene oxide.

REACTIONS OF ETHYLENE OXIDE

Reactions with Water. Hydration of ethylene oxide in aqueous solutions containing 0.5 per cent sulphuric acid (as catalyst) has been investigated by Matignon, Moureu and Dode.[40] They found the products included the following glycols: ethylene glycol, b.p. 197°C. (97°C. at 14 mm.), d_4^{15} 1.1170 and n_D^{15} 1.4332; diethylene glycol, b.p. 244.5°C. (133°C. at 14 mm.), d_4^{15} 1.1197 and n_D^{15} 1.4488; triethylene glycol, b.p. 285°C. (165°C. at 14 mm.), d_4^{15} 1.1274 and n_D^{15} 1.4578, and tetraethylene glycol, b.p. 328°C. (198°C. at 14 mm.), d_4^{15} 1.1285 and n_D^{15} 1.4609. The relative proportions of these substances were considered to depend upon the ratio of ethylene oxide to water in the reaction mixtures and were only slightly changed by variations in reaction temperature (within the range 50-90°C.) or in acid concentration (within the limits 0.5 to 5.0 per cent sulphuric acid). The influence of ethylene oxide-water ratio on the proportions of products in a series of experiments carried out at 90-95°C. is shown in Table 120.

TABLE 120.—*Hydration of Ethylene Oxide at 90-95°C.*

Moles of Water Per One Mole of Ethylene Oxide	Per Cent of Individual Products on Ethylene Oxide Used Ethylene Glycol	Diethylene Glycol	Triethylene Glycol	Tetraethylene Glycol	Higher Glycols
10.5	82.3	12.7			
4.2	65.7	27.0	2.3		
2.1	47.2	34.5	13.0	0.3	
0.61	15.7	26.0	19.8	19.0	14.5

Reaction with Hydroxylated Organic Compounds. The action of ethylene oxide on the lower aliphatic alcohols forms the basis of a well-known method for the manufacture of glycol monoalkyl ethers.[41] The process may be effectively catalyzed by acidified hydrosilicates, such as aluminum hydrosilicate,[42] and also by fluorine compounds such as boron trifluoride. An 80 per cent yield of ethylene glycol monoisopropyl ether is said to be possible on heating isopropyl alcohol and ethylene oxide with boron trifluoride.[43] This type of reaction can, however, be carried out in the absence of catalysts by heating the reactants at a sufficiently high temperature.

In a process disclosed by Wittwer,[44] ethylene oxide and an alcohol such as ethanol are passed continuously through a reaction vessel heated to above 130°C. under sufficient pressure to maintain liquid-phase conditions. However, etherification does not stop at formation of simple glycol monoether, but, if sufficient ethylene oxide is present, monoethers of the higher glycols are formed by further condensation. Thus, combinations of aliphatic monohydric alcohols of more than 7 carbon atoms with 2 or 3 moles of ethylene oxide may occur at 120-160°C. in the presence of caustic soda or caustic potash. Yields consist of the corresponding ethers of di- and triethylene glycols. Such substances are reported to be of value in the textile, leather, paper, lacquer, pharmaceutical and cosmetic industries as wetting, emulsifying, penetrating and softening agents.[45] The monooleyl ether of triethylene glycol, prepared from oleyl alcohol and the requisite amount of ethylene oxide, is said to furnish stable aqueous emulsions of oils or fats. Polyolefin glycol ethers made by the action of olefin oxides on alcohols or on glycol monoethers are suggested as solvents for nitrocellulose and other cellulose esters.[46]

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[38] O. F. Lubatti, *J.S.C.I.*, 1935, **54**, 424T; *Chem. Abs.*, 1936, **30**, 1689; *Brit. Chem. Abs.* **B**, 1936, 77.

[39] This apparatus is described by A. B. P. Page, *J.S.C.I.*, 1932, **51**, 369T; *Chem. Abs.*, 1933, **27**, 792; *Brit. Chem. Abs.* **B**, 1933, 94. See also *J.S.C.I.* 1935, **54**, 421T; *Chem. Abs.*, 1936, **30**, 1689.

[40] C. Matignon, H. Moureu and M. Dole, *Bull. soc. chim.*, 1934, (5) 1, 1308; *Brit. Chem. Abs.* **A**, 1935, 63; *Chem. Abs.*, 1935, **29**, 1777.

[41] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934, 537.

[42] H. Dehnert and W. Krey, U. S. P. 1,996,003, Mar. 26, 1935, to I. G. Farbenind. A. G.; *Chem. Abs.*, 1935, **29**, 3349.

[43] G. Steimmig and K. Baur, German P. 578,722, 1933 (addition to German P. 558,646, 1930; *Chem. Abs.*, 1933, **27**, 512), to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934 **28**, 784.

[44] M. Wittwer, U. S. P. 1,976,677, Oct. 9, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934 **28**, 7263. German P. 595,174, 1934; *Chem. Abs.*, 1934, **28**, 4067.

Zimakov and Churakov[47] recommend a 1:8 mixture of oxide and absolute alcohol heated in an autoclave with 1 per cent sulphuric acid for 7 to 8 hours at 100°C. The reaction period may be reduced to 3 hours by raising the temperature to 300°C. There was almost no formation of ethylene glycol or ethers of polyglycols. Yields of the monoethyl ether ranged from 95 to 99 per cent. On a commercial scale, using 95 per cent alcohol in 5:1 mixture with ethylene oxide and one-half of one per cent of acid catalyst the following products resulted from interaction at 150°C. for 5 hours: 35 to 40 per cent monoethyl ether of ethylene glycol, 55 to 60 per cent of ethylene glycol and 0.5 per cent mixed ethers. The dehydrating action of the ethylene oxide on the alcohol made possible the recovery of two-thirds of the alcohol in anhydrous form.

By the reaction of ethylene oxide with polyhydric alcohols, a wide variety of hydroxyethyl ethers may be readily prepared. A product, said to be useful as a dressing oil for cotton, may be obtained by heating diethylene glycol with 4 or more moles of ethylene oxide in the presence of nickel sulphate.[48] Hydroxy compounds resulting from condensation of alkene oxides with polyhydric alcohols may be esterified with higher aliphatic acids to furnish water-soluble esters useful as emulsifying agents in admixture with sulphonated higher aliphatic alcohols or their derivatives.[49] Some of the hydroxyethyl ethers of the higher polyhydric alcohols, such as pentaerythritol, sorbitol and hexitols, have been described by Schmidt and Meyer,[50] who recommend these substances and their esters as wetting, cleansing or dispersing agents in the textile industry.

The action of ethylene oxide on cellulose has been studied by Nikitin and Rudneva.[51] They found bleached cotton wool to react with ethylene oxide at 50°C. to yield a product containing only one hydroxyethyl group per 32 cellulose units of $C_6H_{10}O_5$. In the presence of dilute alkalies the degree of etherification was increased to 1 ether group per 4 to 8 cellulose units. A maximum etherification, namely, 1 ether per 1.5 cellulose units, was attained with 18 per cent caustic soda, or 35 per cent caustic potash, at 50-60°C. for 15 minutes. The products, which yielded solutions (in caustic soda) of increasing viscosity with the degree of etherification, were much more readily hydrolyzed and acetylated than cellulose.

[45] British P. 404,931, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 4549; *Brit. Chem. Abs.* **B**, 1934, 266.

[46] German P. 608,478, 1935, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, **29**, 2741.

[47] P. Zimakov and A. Churakov, *Org. Chem. Ind.* (*U.S.S.R.*), 1936, 1, 329; *Chem. Abs.*, 1936, **30**, 7540. See also British P. 271,169, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1928, **22**, 1596; *Brit. Chem. Abs.* **B**, 1927, 571.

[48] C. Schöller and M. Wittwer, German P. 605,973, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 2000.

[49] K. Marx, K. Brodersen and M. Zabel, German P. 626,491, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 3548.

[50] O. Schmidt and E. Meyer, U. S. P. 1,959,930, May 22, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 4430. Also O. Schmidt and E. Meyer, German P. 598,596 and 599,580, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5832.

[51] N. I. Nikitin and T. I. Rudneva, *J. Applied Chem.* (*U.S.S.R.*), 1935, **8**, 1023; *Brit. Chem. Abs.* **A**, 1936, 57; *Chem. Abs.*, 1936, **30**, 5408.

Etherification of natural or artificial cellulosic textiles by alkene oxides in aqueous alkali of at least 11 per cent strength has been proposed by Lawrie, Reynolds and Piggott.[52] The type of finish obtained is determined by the oxide-cellulose unit ratio. For example, 0.3-1.0 mole of oxide produces an organdie, but 1-1.5 give a parchment appearance. Schorger[53] describes the manufacture of hydroxyalkyl ethers of cellulose by treating mercerized cellulose (freed from excess alkali lye by squeezing) with ethylene oxide, or other 1,2-oxides, or chlorohydrins, at below 45°C. With 11 to 20 per cent of ethylene oxide at 0°C. the products are soluble in 10 per cent aqueous alkali. Those obtained with less than 11 per cent of the oxide become soluble in this strength of alkali at about −20°C. although tending to form gels when the solution is warmed. Dreyfus[54] prepares hydroxyalkylcellulose by reacting an alkene oxide, or a chlorohydrin, with cellulose in the presence of a primary or secondary organic base containing at least one alkyl, aralkyl or alicyclic radical free from hydroxyl groups, such as diethylamine. Etherification of cellulose by means of gaseous alkene oxides at about 120°C. in the presence of weak acids or caustic alkalies or other basic substances, has also been suggested.[55] In another process proposed by Dreyfus,[56] cellulose is reacted with alkene oxides at pressures of at least 5 atmospheres and at temperatures such that the alkene oxide is either wholly liquid or partially or wholly gaseous, to yield hydroxyalkyl ethers for use as sizes, dressings and finishes for textiles. Etherification of partially esterified cellulose by alkene oxides in the absence of strong inorganic bases and under conditions such that no substantial saponification occurs, has also been suggested.[57]

Hydroxyethyl-lignin has been obtained by Nikitin and Rudneva[58] as an amorphous solid having greater hygroscopicity and swelling capacity than lignin. The product was made by treating Willstatter lignin[58a] with ethylene oxide and 18 per cent aqueous caustic soda at 70°C. for 24 hours, for 2 hours at 70-72°C. or for 2 days at room temperature. The crude lignin ether was then separated by means of water, washed with alcohol and ethyl ether and finally dried. On hydrolysis for 5 hours with 5 per cent sulphuric acid a pure lignin hydroxyethyl ether was obtained. It is an amorphous, insoluble material, having 38.76 per cent of the group $—OCH_2CH_2OH$ and 5.18 per cent of HO— group that may be acetylated. The former group may be removed by hydrogen iodide at 135-140°C., but is not affected by boiling with 5 per cent sulphuric acid. Such behavior is considered due to presence of a simple ether bond. It was believed that lignin reacted with ethylene oxide as indicated in the following scheme suggested by Shoruigin and Ruimashevskaya.[59]

$$R—OH + (CH_2)_2O \longrightarrow R—O—CH_2—CH_2—OH$$

Reaction with Hydrogen Halides and Metallic Halides. Ethylene oxide combines energetically with hydrogen chloride, even in aqueous solution.

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[52] L. G. Lawrie, R. J. W. Reynolds and H. Piggott, British P. 439,880, 1935, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1936, **30**, 3661; *Brit. Chem. Abs.* **B**, 1936, 272.

[53] A. W. Schorger, U. S. P. 1,941,276, 1,941,277 and 1,941,278, Dec. 26, 1933, to C. F. Burgess Laboratories, Inc.; *Brit. Chem. Abs.* **B**, 1934, 879; *Chem. Abs.*, 1934, **28**, 1861.

[54] H. Dreyfus, British P. 397,116, 1933; *Chem. Abs.*, 1934, **28**, 893. Also U. S. P. 2,033,126, Mar. 10, 1936; *Chem. Abs.*, 1936, **30**, 3232.

[55] H. Dreyfus, British P. 415,382, 1934; *Chem. Abs.* 1935, **29**, 925; *Brit. Chem. Abs.* **B**, 1934, 956. U. S. P. 2,055,892, Sept. 29, 1936, *Chem. Abs.*, 1936, **30**, 8615.

[56] H. Dreyfus, British P. 415,383, 1934; *Chem. Abs.*, 1935, **29**, 925; *Brit. Chem. Abs.* **B**, 1931, 956. U. S. P. 2,055,893, Sept. 29, 1936, *Chem. Abs.*, 1936, **30**, 8615.

[57] H. Dreyfus, British P. 396,796, 1933; *Chem. Abs.*, 1934, **28**, 484, *Brit. Chem. Abs.* **B**, 1933, 860.

[58] N. I. Nikitin and T. I. Rudneva, *J. Applied Chem.* (*U. S. S. R.*), 1935, **8**, 1176; *Brit. Chem. Abs.* **A**, 1936, 340; *Chem. Abs.*, 1936, **30**, 6557.

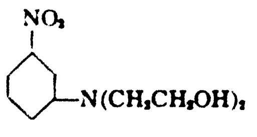
[58a] R. Willstatter and L. Kalb, *Ber.*, 1922, **55**, 2637; *Chem. Abs.*, 1923, **17**, 982; *J.S.C.I.*, 1922, **41**, 893A. See also Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**, 747.

[59] P. P. Shoruigin and I. Ruimashevskaya, *Ber.*, 1933, **66**, 1014; *Chem. Abs.*, 1933, **27**, 4529.

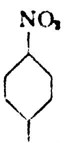
with the formation of ethylene chlorohydrin. Preparation of the latter from the oxide and liquid hydrogen chloride has been described by Gebauer-Fuelnegg and Moffett.[60] Thus, hydrogen chloride present as impurity in tetraethyl silicate preparations[61] may be removed by addition of the alkene oxide.

It has long been known that aqueous solutions of certain metallic chlorides, such as those of zinc, manganese and magnesium, are decomposed by ethylene oxide with the formation of ethylene chlorohydrin and a precipitate of the metallic hydroxide or oxychloride. This reaction has been utilized by Ziese[62] for the preparation of sols and reversible gels of hydrated metallic oxides. For example, addition of ethylene oxide to aluminum chloride in aqueous solution yields ethylene chlorohydrin and aluminum hydroxide. The latter remains as a sol until about 90 per cent of the theoretical amount of ethylene oxide has been added, after which solidification to a clear gel occurs. By-products can be removed from the sol by extraction with solvents (for the chlorohydrin) or by distillation. The sols obtained from solutions of aluminum, chromium, zinc and thorium halides, which may be regarded as containing highly basic salts, may be dried to reversible gels; the latter can be again converted into stable sols when contacted with water, ethyl alcohol or glycerol. The metal oxide hydrates are precipitated as gels, without passage through a hydrosol phase, by the use of ethylene oxide in excess. In the case of bivalent metals, such as zinc or manganese, precipitation often occurs in the presence of quite small amounts of ethylene oxide owing to the instability of the sol phase. Bromides and iodides can be used in place of chlorides; propene oxide instead of ethylene oxide. Water may be replaced by 96 per cent ethyl alcohol.

Reaction with Organic Bases. Ethylene oxide reacts readily with a large number of primary and secondary organic bases with the production of the corresponding hydroxyethylamine. Thus, by heating equimolecular proportions of dibenzylamine, water and ethylene oxide in a sealed tube at 100°C., Gabel[63] obtained a 25 per cent yield of β-dibenzylaminoethyl alcohol, m.p. 45.5-47°C. Under similar conditions the alkene oxide and water (1 mole each) react with *m*-phenylenediamine at 30°C. to give after 8 hours a 31 per cent yield of β-*p*-aminophenylaminoethyl alcohol, $HOCH_2CH_2NHC_6H_4NH_2$, m.p. 52-53°C.[64] The compound is soluble in alcohol, acetone and water, but less so in ethyl ether and benzene. On standing it resinifies. It is said[65] that nitroarylamines, on heating with 2 molecular proportions of ethylene oxide at 140-170°C., are converted into their NN-di-β-hydroxyethyl derivatives. Similar derivatives of *m*-nitroaniline and *p*-nitroaniline have constitutions represented by the following formulas:



m.p. 98-99°C.



m.p. 101-102°C.

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[60] E. Gebauer-Fuelnegg and E. Moffett, *J.A.C.S.*, 1934, **56**, 2009; *Chem. Abs.*, 1934, **28**, 6698; *Brit. Chem. Abs.* **A**, 1934, 1200.

[61] P. L. Salzberg, U. S. P. 1,944,274, Jan. 23, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 2012; *Brit. Chem. Abs.* **B**, 1934, 954.

[62] W. Ziese, *Ber.*, 1933, **66**, 1965; *Brit. Chem. Abs.* **A**, 1934, 142; *Chem. Abs.*, 1934, **28**, 1245. W. Ziese and K. Pfaff, U. S. P. 1,951,718, Mar. 20, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 3499. British P. 417,340, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1182; *Brit. Chem. Abs.* **B**, 1935, 226.

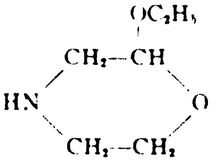
[63] Yu. O. Gabel, *Bull. soc. chim.*, 1934, (5) 1, 1006; *Brit. Chem. Abs.* **A**, 1934, 1215; *Chem. Abs.*, 1935, **29**, 750.

[64] O. Gabel and R. M. Matzkevich, *Ukrain. Chem. J.*, 1935, **10**, 4; *Brit. Chem. Abs.* **A**, 1935, 969; *Chem. Abs.*, 1935, **29**, 7957.

[65] British P. 410,707, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1934, 617.

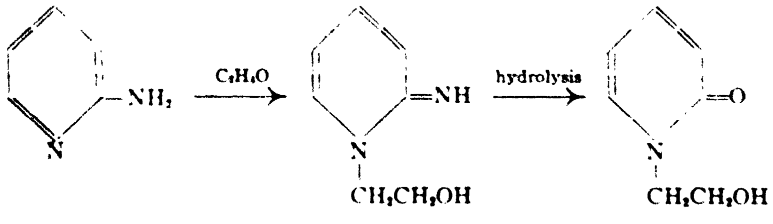
Secondary aromatic bases of the type of β,γ-dihydroxypropylaniline,[66] or their γ-alkyl ethers,[67] may be converted into the corresponding N-β-hydroxyethyl derivatives by heating with ethylene oxide under pressure at about 150-160°C. Ruberg and Shriner[68] have described the condensation of a number of aliphatic secondary amines with ethylene oxide at below 60°C. to yield mixtures of alcohols of the types $NR_2CH_2CH_2OH$ and $NR_2(CH_2CH_2O)_nH$, in which R is an aliphatic radical. These can be reacted with nitrobenzoyl chloride to give the corresponding nitrobenzoates which in turn may be reduced to the respective aminobenzoates. The latter have possible applications as local anesthetics. It was noted, however, that although this property increased with the molecular weights of the substances, nevertheless their toxicity also became greater.

In the absence of water many of the well-known reactions of ethylene oxide with the simple primary and secondary bases do not take place at all or only very slowly. Knorr[69] has shown, for example, that ethylene oxide does not react with carefully dried 2-aminoacetaldehyde. In the presence of water, however, complete combination occurs and the product, on standing, loses water with the formation of a substance (b.p. 253°C.) which is probably 5-ethoxymorpholine,



Nearly theoretical yields of tertiary alkylolarylamines are said[70] to be obtained by heating a secondary alkylarylamine with an alkene oxide in a closed vessel at 140-150°C. The products exemplified by 1-(phenylethylol)-butane may be used as dye intermediates.

An unusual rearrangement occurs during the condensation of 2-aminopyridine and dry ethylene oxide in methyl alcohol at 15-20°C. Under these conditions the formation of 1-β-hydroxyethylpyridoneimine takes place.[71] This substance may be readily hydrolyzed to the corresponding pyridone compound by boiling with 10 per cent caustic soda solution. The changes may be indicated thus:



Natural polymeric aliphatic amino compounds, such as casein, horn, wool, glue or albuminous materials, may be reacted with ethylene or propene oxide in a slightly alkaline aqueous medium.[72] Such alkoxy derivatives are not decomposed by fermentation and may be used for emulsifying fats and waxes. They may be reduced by catalytic hydrogenation. In another procedure, casein is treated in aqueous suspension (neutral or weakly acidic with acetic or other organic acids) at 40-90°C. with an alkene oxide. The products are insoluble in water and weak aqueous alkalies but soluble in dilute acids. They may be used as adhesives, sizing and finishing agents and for molding.[73]

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[66] British P 409,238, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs* **B**, 1934, 535.

[67] British P. 409,237, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1934, 535.

[68] L. A. Ruberg and R. L. Shriner, *J.A.C.S.*, 1935, **57**, 1581; *Brit. Chem. Abs.* **A**, 1935, 1363; *Chem Abs.*, 1935, **29**, 7306.

[69] L. Knorr, *Ber.*, 1899, **32**, 729; *J.C.S.*, 1899, **76** (1), 461.

[70] W. Müller, U. S. P. 1,930,858, Oct. 17, 1933, to General Aniline Works; *Chem. Abs.*, 1934, **28**, 173.

[71] I. L. Knunyantz, *Ber.*, 1935, **68**, 397; *Brit. Chem. Abs.* **A**, 1935, 627. *Compt. rend. acad. sci. U.R.S.S.*, 1935, **1**, 501; *Brit. Chem. Abs.* **A**, 1935, 757; *Chem. Abs.*, 1935, **29**, 3339.

[72] K. Sponsel and H. Krauss, U. S. P. 1,965,008, July 3, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5079.

An interesting development in the reaction between alkene oxides and organic nitrogen compounds is the observation that carboxyl- or sulphonamides, with at least one replaceable hydrogen atom and a radical of at least 8 carbon atoms, may undergo condensation with up to 3 moles of an oxide for each replaceable hydrogen atom, in the presence of an alkaline catalyst. For example, dibutylnaphthalenesulphonamide reacts with ethylene oxide to yield a product having dispersing, emulsifying and wetting properties. Moreover, the products obtained may form with polybasic acids combinations having acid functions.[74] Combination of ethylene oxide, either alone or in non-hydroxylic media, with a primary, secondary or tertiary water-soluble amine or with a primary or secondary acylated water-soluble amine having at least two hydroxyl groups, has also been described.[75] Such materials are suggested as wetting and other agents for use in the treatment of textiles. Similar auxiliary agents are prepared by heating ethylene oxide with the condensation products of polyhydroxylated primary or secondary aliphatic amines (such as methyl glucamine) and higher aliphatic acids.[76]

Polymerization of Ethylene Oxide. Ethylene oxide (and propene oxide) undergo polymerization beyond the dimer stage when subjected to the action of caustic potash or other alkali or alkaline-earth metal compounds in the presence of an inert organic liquid medium. In most instances temperatures of 110-130°C. have been found effective.[77] Polymers of ethylene or propene oxide may be employed as the liquid if in a low degree of polymerization. The latter undergo further condensation so that a homogeneous product is formed.[78]

By the slow polymerization of ethylene oxide at ordinary temperature under the influence of strontium, calcium and zinc oxides, or carbonates, Staudinger and Lohmann[79] prepared eucolloidal products having mean molecular weights of 100,000 or over, whereas previous experiments with other catalysts had yielded polymers of molecular weight not exceeding 12,000. Sluggish action is necessary for this change, the type of transformation depending on the catalyst. Oxides of iron, magnesium and lead, as well as silica gel and carbon, were without effect, but alumina slowly yielded hemicolloids. Best results followed use of zinc oxide, which was easily removed without affecting the products. All polyethylene oxides were crystalline. A "meandering" form of the molecule has been postulated which explains the solubility and low melting points of the compounds in contrast with the polyoxymethylenes and the paraffins.[80]

[73] R. Bauer and G. Mauthe, U. S. P. 1,979,601, Nov. 6, 1934, to I. G. Farbenind. A. G., *Chem. Abs.*, 1935, **29**, 254. Also British P. 419,675, 1933; *Brit. Chem. Abs.* **B**, 1935, 91, *Chem. Abs.*, 1935, **29**, 2623. German P. 574,841, 1933; *Chem. Abs.*, 1934, **28**, 1485.

[74] British P. 415,718, 1933; *Brit. Chem. Abs.* **B**, 1934, 954, *Chem. Abs.*, 1935, **29**, 1519. French P. 751,641, 1933; *Chem. Abs.*, 1934, **28**, 868. British P. 420,545, 1934; *Chem. Abs.*, 1935, **29**, 3427; *Brit. Chem. Abs.* **B**, 1935, 139. All patents to I. G. Farbenind. A.-G.

[75] French P. 768,732, 1934, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1935, **29**, 621.

[76] French P. 770,294, 1934, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1935, **29**, 622.

[77] M. Wittwer, U. S. P. 1,976,678, Oct. 9, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 7261.

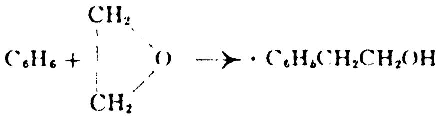
[78] British P. 406,443, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 4743; *Brit. Chem. Abs.* **B**, 1934, 393.

[79] H. Staudinger and H. Lohmann, *Ann.*, 1933, **505**, 41; *Chem. Zentr.*, 1934, I, 1027; *Chem. Abs.*, 1933, **27**, 4790; *Brit. Chem. Abs.* **A**, 1933, 932.

[80] For a discussion of the structure of ethylene oxide polymers, see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935, 990.

The structure of the polyethylene oxides has been investigated by Sauter,[81] using x-ray methods.

Reaction with Aromatic Hydrocarbons. In the presence of appropriate catalysts, ethylene oxide may be condensed with aromatic hydrocarbons to give the corresponding β-arylethyl alcohols, usually in poor yield. In the case of benzene, the product is phenylethyl alcohol (phenethyl alcohol). The reaction may be represented as follows:



$$C_6H_6 + \begin{array}{l} CH_2 \\ | \quad \rangle O \\ CH_2 \end{array} \longrightarrow C_6H_5CH_2CH_2OH$$

Condensation of alkene oxides with hydrocarbons such as benzene in the presence of a Friedel-Crafts catalyst, a non-substituted heterocyclic compound (e.g., pyridine or quinoline) or a monohalogen derivative such as monochlorobenzene, at temperatures up to 100°C., has been suggested by Hopff.[82] In making phenethyl alcohol, the temperature is best maintained at 5°C. Further details of the influence of temperature on the condensation of ethylene oxide with benzene in the presence of aluminum chloride or ferric chloride are given by Klipstein.[83] The latter states that bibenzyl, which is produced at the higher operating temperatures, is formed only to a negligible extent at temperatures of about 5-6°C., when the yield of phenethyl alcohol amounts to 65 per cent of the theoretical. Low temperatures (0 to 10°C.) are recommended also by Theimer.[84] Carpenter[85] proposes to employ an acid-condensing agent (aluminum chloride) in an amount at least 3 to 4 times that of the aliphatic oxide used. He further provides for removal of hydrogen chloride in a stream of air or inert gas.

According to Valik and Valik,[86] loss of ethylene oxide as chlorohydrin can be minimized by diluting the gaseous oxide with an inert diluent such as air, nitrogen or carbon dioxide. The process may then be carried out at 5-10°C. in the presence of ammonia or an amine, such as triethanolamine, to take up the free hydrogen chloride.

Alkene oxides may be converted into aralkyl alcohols by reaction with metal compounds of certain aromatic hydrocarbons.[87] Thus, combination of ethylene oxide with phenyl sodium in toluene suspension at −50°C. gives phenethyl alcohol. β-*p*-Tolylethyl alcohol (b.p. 113-117°C. at 11 mm.) is produced in a similar manner from *p*-tolyl sodium.

Reaction with Hydrogen Sulphide and Mercaptans. Chichibabin and Bestuzhev[88] observed that combination of equimolecular proportions of ethylene oxide and hydrogen sulphide takes place slowly in aqueous solution at 8-10°C. After 10 days a quantitative yield of thioethylene glycol, b.p. 54°C. at 12 mm., was obtained. With twice as much of the oxide in a cooled dilute solution, the product was thiodiethylene glycol, b.p. 130°C. at 2 mm. A mixture of viscous polyglycol sulphides resulted in the absence of cooling. With 3 moles of ethylene oxide in dilute solution, hydrogen sulphide combined to give the strongly basic triethylolsulphonium hydroxide. These reactions, which are catalyzed by mineral acids, chlorides of aluminum or heavy metals, may be represented by the scheme:

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[81] E. Sauter, *Z. physik. Chem.*, 1933, **21**, 161, 186; *Chem. Zentr.*, 1934, I, 1025; *Chem. Abs.*, 1933, **27**, 3867; *Brit. Chem. Abs.* **A**, 1933, 666.

[82] H. Hopff, U. S. P. 2,029,618, Feb. 4, 1936, to I. G. Farbenind. A.G.; *Chem. Abs.*, 1936, **30**, 1805. German P. 594,968, 1934; *Chem. Abs.*, 1934, **28**, 5077.

[83] K. H. Klipstein, Canadian P. 340,555, 1934, to E. C. Klipstein and Sons Co., to The Calco Chemical Co. Inc.; *Chem. Abs.*, 1934, **28**, 4067.

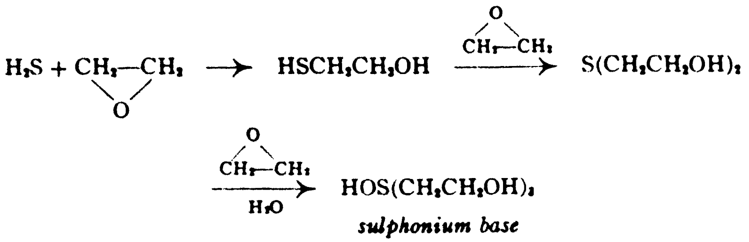
[84] E. T. Theimer, U. S. P. 2,047,396, July 14, 1936, to Van Amerigen Haebler, Inc.; *Chem. Abs.*, 1936, **30**, 6005.

[85] M. S. Carpenter, U. S. P. 2,013,710, Sept. 10, 1935, to Givaudan-Delawanna, Inc.; *Chem. Abs.*, 1935, **29**, 6901; *Brit. Chem. Abs.* **B**, 1936, 974.

[86] L. Valik and I. Valik, British P. 398,136, 1933; *Chem. Abs.*, 1934, **28**, 1047; *Brit. Chem. Abs.* **B**, 1933, 956.

[87] E. Dorrer and H. Hopff, German P. 596,523, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5077. See also British P. 399,258, 1932; *Brit. Chem. Abs.* **B**, 1933, 999. French P. 752,478, 1933; *Chem. Abs.*, 1934, **28**, 1047.

[88] A. E. Chichibabin and M. A. Bestuzhev, *Compt. rend.*, 1935, **200**, 242; *Chem. Abs.*, 1935, **29**, 2509; *Brit. Chem. Abs.* **B**, 1935, 606.



The production of thiomono- and thiodiethylene glycols and triethylolsulphonium hydrate by direct combination of hydrogen sulphide and ethylene oxide at different temperatures and pressures has been previously reported by Chichibabin.[89] In this case the reaction was said to be favored by the presence of water, lower alcohols and catalysts such as porous clay or alumina.

Thiodiethylene glycol in 90 per cent yield was secured by Nenitzescu and Scarlatescu[90] on passage of a gaseous mixture of 1 mole hydrogen sulphide and 2 moles ethylene oxide through glass beads moistened with the product of reaction. Replacement of the hydrogen sulphide by mercaptans led to formation of the corresponding hydroxyethyl thioethers in good yields. The formulas and properties of some of these substances prepared by Nenitzescu and Scarlatescu are given in Table 121.

TABLE 121.—*Hydroxyethyl Thioethers.*

Oxide Used	Mercaptan	Formula of Product	Boiling Point
Ethylene oxide	Ethyl	$C_2H_5SCH_2CH_2OH$	--
" "	Phenyl	$C_6H_5SCH_2CH_2OH$	119-120°C. at 4 mm.
Cyclohexene oxide	Propyl	$C_3H_7SC_6H_{10}OH$	96- 97°C. at 3 mm.
" "	Phenyl	$C_6H_5SC_6H_{10}OH$	148-149°C. at 4 mm.
" "	Benzyl	$C_6H_5CH_2SC_6H_{10}OH$	158-160°C. at 3 mm.

It has been proposed[91] to condense mercaptans (except those containing the —SH group linked to >CO or a heterocyclic nucleus) with alkene oxides, such as ethylene oxide. It was suggested that groups introduced have at least one ether oxygen atom and not less than 4 carbon atoms. The products are soluble in water and are said to be scouring, dispersing, wetting and emulsifying agents. As an example, dodecyl mercaptan is heated with 5 equivalents of ethylene oxide at 140°C. in the presence of 0.5 per cent of sodium methoxide.

Substitution of inorganic sulphur-containing compounds for mercaptans is reported to furnish thioethers.[92] An example of this is the preparation of diethyl sulphide (b.p. 55-56°C.) from ethylene oxide and potassium thiocyanate. The latter may be replaced by thiourea.

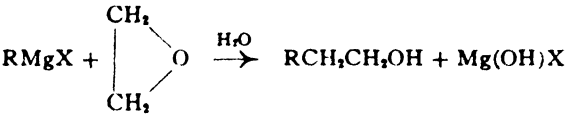
Miscellaneous Reactions. With Grignard reagents, ethylene oxide has been shown to combine with the formation of the corresponding hydroxyethyl derivative according to the equation,

[89] A. E. Chichibabin, French P. 769,216, 1934; *Chem. Abs.*, 1935, 29, 481.

[90] C. D. Nenitzescu and N. Scarlatescu, *Ber.*, 1935, 68, 587; *Chem. Abs.*, 1935, 29, 3979; *Brit. Chem. Abs.* A, 1935, 729.

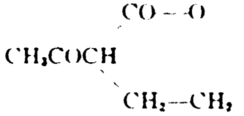
[91] British P. 437,590, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1936, 88.

[92] French P. 797,621, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, 30, 7122.



in which R is an alkyl or aryl radical and X is a halogen. For example, it is proposed[93] to synthesize phenethyl alcohol by reacting phenylmagnesium chloride (obtained by heating chlorobenzene with magnesium at 150-160°C. in the absence of a solvent) with ethylene oxide (or chlorohydrin) in the presence of benzene. This type of reaction has been particularly useful in the preparation of certain acetylenic alcohols by reacting ethylene oxide with the Grignard compounds of monoalkylacetylenes. Faucounau[94] made 3-nonyn-1-ol and 3-decyn-1-ol by this procedure.[95] In this manner 3-octyn-1-ol was obtained by Danehy, Vogt and Nieuwland[96] from hexyne-1 and ethylene oxide. Condensation of 2 moles of the Grignard reagent of heptyne-1 with 1 mole of ethylene oxide was found to yield ethylene bromohydrin and 3-nonyn-1-ol in addition to some unchanged heptyne-1. A similar reaction occurred with the Grignard reagents from phenylacetylene.[97] Bachman[98] calls attention to "the fact that this type of reaction was first reported by Iotsitch[99] who used it to prepare 3-pentyn-1-ol."

Knunyantz, Chelintzev and Osetrova[100] have observed that ethylene oxide combines readily with ethyl sodioacetoacetate in ethyl alcohol solution at 0°C. The product, after decomposition with dilute acetic acid, is 1-aceto-3-butyrolactone,



This compound can be hydrolyzed by warm 5 per cent hydrochloric acid to produce 3-keto-*n*-pentanol-1. Addition of sodium bisulphite to ethylene oxide was accomplished by Lauer and Hill.[100a] The product is reported to be sodium β-hydroxyethanesulphonate, a colorless crystalline compound which melts at 192-194°C.

Uses of Ethylene Oxide

Although the principal application of ethylene oxide is that of a chemical intermediate in the manufacture of solvents such as glycol ethers, the compound itself is widely used as an insecticidal fumigant, particularly in the preservation of stored grain. As employed in fumigation, the oxide is usually admixed with an excess of carbon dioxide, a liquid mixture of 1 part of ethylene oxide and 9 parts of carbon dioxide being marketed for this purpose. For the destruction of insects, Brown[101] recommends the following minimum lethal concentrations per 1000 cu. ft. of room space: 5 lbs. for 3 hours, 3 lbs. for 6 hours, 2 lbs. for 18 hours or 24 hours. The influence of various factors on the efficiency of fumigation by ethylene oxide-carbon dioxide mixtures has been studied by Twinn,[102] who found that this gas penetrated many containers, except boxes wrapped in three layers of Cellophane. In comparing the fumigant with a mixture of ethylene dichloride and carbon tetrachloride, the latter was found to penetrate less readily and to be less agreeable to handle, although it exerted no ill effects on workers even when inhaled in considerable amounts. The advisability and advantages of adding carbon dioxide to ethylene oxide used as a disinfectant of vegetable materials (particularly grain), under partial vacuum or at atmospheric pressure, have been discussed by Lepigre.[103]

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[93] P. P. Shoruigin, V. I. Isagulyantz, A. R. Guseva, K. S. Polyakova and V. P. Osipova, British P. 398,561, 1933; *Brit. Chem. Abs.* **B**, 1933, 956. French P. 738,277, 1932, *Chem. Abs.*, 1933, 27, 1638. Swiss P. 159,939, 1933; *Chem. Abs.*, 1934, **28**, 1365. *Cf.* A. Weissenborn, U. S. P. 2,058,373, Oct. 20, 1936, to Winthrop Chemical Co.; *Chem. Abs.*, 1937, **31**, 118.

[94] L. Faucounau, *Compt. rend.*, 1934, **199**, 605; *Brit. Chem. Abs.* **A**, 1934, 1199; *Chem. Abs.*, 1934, **28**, 7245.

[95] G. B. Bachman, *J.A.C.S.*, 1935, **57**, 382; *Chem. Abs.*, 1935, **29**, 1771; *Brit. Chem. Abs.* **A**, 1935, 470.

[96] J. P. Danehy, R. R. Vogt and J. A. Nieuwland, *J.A.C.S.*, 1934, **56**, 2790; *Chem. Abs.*, 1935, **29**, 725; *Brit. Chem. Abs.* **A**, 1935, 193.

[97] J. P. Danehy, R. R. Vogt and J. A. Nieuwland, *J.A.C.S.*, 1935, **57**, 2327; *Brit. Chem. Abs.* **A**, 1936, 187; *Chem. Abs.*, 1936, **30**, 78.

[98] G. B. Bachman, *loc. cit.*

[99] Iotsitch, *J. Russ. Phys.-Chem. Soc.*, 1907, **39**, 652. *Cf. Bull. soc. chim.*, 1909, IV, 6, 98.

[100] I. L. Knunyantz, G. V. Chelintzev and E. D. Osetrova, *Compt. rend. acad. sci. U.R.S.S.*, 1934, 1, 312; *Chem. Abs.*, 1934, **28**, 4382; *Brit. Chem. Abs.* **A**, 1934, 509.

[100a] W. M. Lauer and A. Hill, *J.A.C.S.*, 1936, **58**, 1873; *Chem. Abs.*, 1936, **30**, 8143.

[101] E. W. Brown, *U. S. Naval Med. Bull.*, 1934, **32**, 294; *Brit. Chem. Abs.* **B**, 1936, 396; *Chem. Abs.*, 1934, **28**, 1144.

In the fumigation of ships and warehouses, the method of vaporization of the liquid fumigant requires careful consideration. This question has been discussed by Page and Lubatti,[104] who recommend that the latent heat requirements of such vaporization should be supplied from an external source. These investigators have described a vaporizer for use in fumigating dried fruit in barges and in similar operations. The effect of ethylene oxide on books and writing papers has been studied by Weber, Shaw and Back.[105] Their tests indicated that this oxide may be used with safety.

Cotton and Young[106] have described the use of solid carbon dioxide and ethylene oxide, carbon disulphide or other fumigants in the treatment of seeds, bulbs and foods for their protection against certain insects. A wet or dry preserving agent, for fruit-trees, vines or cereals, has been suggested by Pfaff and Erlenbach. It was made by treating a solution of cupric chloride with an alkene oxide and removing excess of the latter.[107]

Other proposed uses for ethylene oxide are in the stabilization of aliphatic nitrates (in conjunction with acetone)[108] in the treatment of leguminous vegetable materials for the destruction of their bitter principles[109] and for reducing the nicotine content of tobacco.[110] A liquefied mixture of 5 parts of ethylene oxide and 1 part of methyl alcohol has been suggested[111] as a fuel for portable lighting devices, such as cigarette lighters, the fuel being burned in gaseous form without the employment of a wick.

Emulsifying and dispersing agents may be produced by the action of ethylene oxide on the partially oxidized marine-animal oils that result from the oil-tanning of skins.[112]

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[102] C. R. Twinn, *Quebec Soc. Protection Plants*, 25th and 26th Ann Repts, 1934, 52; *Brit. Chem. Abs.* B, 1935, 1071; *Chem. Abs.*, 1935, **29**, 2622.

[103] A. L. Lepigre, *Bull. soc. encour. ind. nat*, 1934, **133**, 509; *Chem Abs*, 1935, **29**, 4884; *Brit. Chem. Abs.* B, 1934, 1075. *Cf.* P. Vayssieres, *Bull. soc. encour. ind. nat.*, 1934, **133**, 295.

[104] A. B. P. Page and O. F. Lubatti, *J.S.C.I.*, 1935, **54**, 246T; *Brit. Chem Abs* B, 1935, 832, *Chem. Abs.*, 1935, **29**, 6326.

[105] C. G. Weber, M. B. Shaw and E. A. Back, *J. Res. Natl. Bur Standards*, 1935, **15**, 271 (Research Paper No. 828); *Chem. Abs.*, 1936, **30**, 188.

[106] R. T. Cotton and H. D. Young, U. S. P. 2,024,027, Dec. 10, 1935, to Government and People of U. S.; *Chem. Abs.*, 1936, **30**, 1174; *Brit. Chem. Abs.* B, 1936, 1062.

[107] K. Pfaff and M. Erlenbach, German P. 578,972, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 852.

[108] J. H. Werntz, Canadian P. 336,584, 1933, to Canadian Industries Ltd.; *Chem. Abs.*, 1934, **28**, 1718.

[109] British P. 424,590, 1933, to Henkel & Co. G.m.b.H.; *Brit. Chem. Abs.* B, 1935, 477; *Chem. Abs.*, 1935, **29**, 5196. French P. 769,932, 1934; *Chem. Abs*, 1935, **29**, 519.

[110] P. M. Gross and L. F. Dixon, U. S. P. 1,962,145, June 12, 1934, to Hall Tobacco Chemical Co.; *Brit. Chem. Abs.* B, 1935, 924; *Chem. Abs.*, 1934, **28**, 4842. French P. 784,795, 1935; *Chem. Abs.*, 1936, **30**, 576.

[111] T. H. Fisher, U. S. P. 1,895,032, Jan. 24, 1933; *Brit Chem. Abs.* B, 1934, 9; *Chem. Abs.*, 1933, **27**, 2559.

[112] H. A. Piggott and G. S. J. White, U. S. P. 2,049,512, Aug. 4, 1936, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1936, **30**, 6476.

ETHANOLAMINES

Alkene oxides combine with ammonia and with primary or secondary organic bases with the formation of hydroxyalkylamines or alkylolamines. The three main products of the reaction between ethylene oxide and ammonia, in aqueous solution, are:

Monoethanolamine	$NH_2CH_2CH_2OH$
Diethanolamine	$NH(CH_2CH_2OH)_2$
Triethanolamine	$N(CH_2CH_2OH)_3$

This addition, however, does not necessarily end with the formation of triethanolamine, since the hydroxyl groups of the latter compound can undergo further reaction with ethylene oxide to yield complex hydroxyethyl ethers of triethanolamine.[113] In general, all three of the simple ethanolamines are obtained simultaneously by reaction of ethylene oxide with strong aqueous ammonia, a large excess of ammonia tending to favor formation of monoethanolamine. However, triethanolamine is the main product when approximately equimolar proportions of ethylene oxide and ammonia are used.

Kautter[114] proposes to treat 1 mole of ethylene oxide with 1 to at least 20 of ammonia, the reaction being carried out at elevated temperatures and pressures, if necessary. Thus, an 83.2 per cent yield of monoethanolamine is prepared by heating a mixture of 88 g. of ethylene oxide and 6 liters of 18.3 per cent aqueous ammonia at 94°C. for 1 hour, the pressure being about 36 lb. per sq. in. At the end of this period, excess ammonia is removed by release of pressure and absorbed in water. The residual liquid is distilled to recover the monoethanolamine. An apparatus for effecting the production of ethanolamines has been described by Reid and Lewis.[115] It consists of porous tubes through which ethylene oxide is passed into aqueous ammonia. The latter is continuously circulated through a heat exchanger to maintain a reaction temperature of 40-50°C. Excess of ammonia and water may be separated by distillation, leaving a residue of triethanolamine that contains 25 to 35 per cent of diethanolamine.

In experiments carried out on a semi-commercial scale, Kedrinskii and Plaska[116] fed ethylene oxide and ammonia in stoichiometrical proportions into a reacting zone filled with a solvent medium. Compressed air was utilized to force the mixture through the solvent, an oxide velocity of 320 g. per liter of solvent being maintained at a temperature of 60°C. The final product consisted of 1.5 per cent di-, 75 per cent triethanolamine and 13 per cent polymerized material with traces of the monoamine and nearly 10 per cent of water. The yield amounted to 1008 g. per 1000 g. ethylene oxide or 89 per cent of theory.

Pure triethanolamine has been recovered from the technical product in the following manner by Germann and Knight.[117] The crude material is first acidified with a slight excess of concentrated hydrochloric acid at 10-15°C. After standing for 1 hour, 70 per cent of the pure hydrochloride separates out and can be filtered, washed with ethyl alcohol (or isopropyl alcohol) and decomposed with caustic soda in isopropyl alcohol solution. The base recovered by vacuum distillation, b.p. 194-195°C. at 10 mm. and d_{20}^{20} 1.1239, is 99 per cent triethanolamine. The solubility of its hydrochloride in isopropyl and ethyl alcohols at 65°C. is 1.1 and 3 g. per liter, respectively .

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[113] For a discussion of the reaction between ammonia and ethylene oxide, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[114] C. T. Kautter, U. S. P. 2,051,486, Aug. 18, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 6759. Canadian P. 356,624, 1936; *Chem. Abs.*, 1936, **30**, 2986. See also British P. 448,373, 1935, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1936, 780, *Chem. Abs.*, 1936, **30**, 7583; *J. Inst. Pet. Tech.*, 1936, **22**, 411A.

[115] E. W. Reid and D. C. Lewis, U. S. P. 1,904,013, April 18, 1933, to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1933, 998; *Chem. Abs.*, 1933, **27**, 3222.

[116] V. Kedrinskii and Kh. Plaska, *Novosti Nefteperérabotki*, 1936, **3**, No. 4, 6; *Chem. Abs.*, 1936, **30**, 6706.

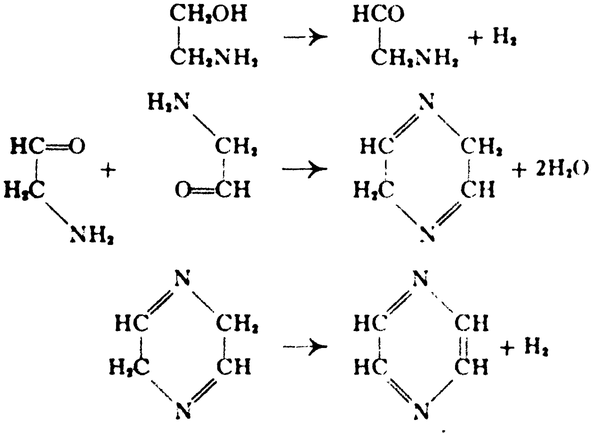
[117] F. E. E. Germann and O. S. Knight, *J.A.C.S.*, 1933, **55**, 4150; *Brit. Chem. Abs.* **A**, 1933, 1280; *Chem. Abs.*, 1933, **27**, 5719.

Properties of Ethanolamines. The ethanolamines are weak bases and yield readily hydrolyzable salts with many weak acids. In other chemical properties, however, they exhibit important differences.

When monoethanolamine is heated with diethyl sulphate, at temperatures not over 200°C., the hydrogen atoms of the amino-group are displaced by ethyl radicals, with the formation of diethylaminoethanol.[118] The method is applicable for the production of other dialkylamino alcohols.

Monoethanolamine and similar aliphatic amines have been found to function as catalysts for the production of ethers of the polyalkene glycols by the action of alkene oxides on polyhydroxy alcohol derivatives.[119] For example, the monoethyl ether of triethylene glycol is formed by treating the corresponding diethylene compound with ethylene oxide.

Monoethanolamine vapor undergoes partial dehydrogenation and condensation in contact with dehydrogenating catalysts, such as finely divided copper or zinc oxide·(containing 4.5 per cent sodium carbonate), at 300°C. In this way Aston, Peterson and Holowchak[120] obtained a 5.6 per cent yield of pyrazine, a cyclic base, b.p. 112-114°C. at 730 mm., evidently produced in the following way:



pyrazine

The gas collected in the runs with the reduced copper activator was exclusively hydrogen. The yield of pyrazine was isolated as the mercuric chloride double salt, $C_4H_4N_2 \cdot HgCl_2$. The catalyst was eventually rendered inactive by resins which Aston and his associates thought were formed by side reactions from the amino-acetaldehyde. In the absence of a catalytic medium the ethanolamine was quite stable at 300°C. Another base, namely, ethylenimine, C_2H_4NH, b.p. 55-56.5°C., can be prepared by heating the acid sulphate of monoethanolamine to 250°C. and subsequently distilling the resulting product with 40 per cent caustic soda.[121]

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[118] French P. 792,046, 1935, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1936, **30**, 4176. G. A. Perkins and J. H. Purse, British P. 451,630, 1936; *Chem. Abs.*, 1937, **31**, 416; *Brit. Chem. Abs.* B, 1936, 1081.

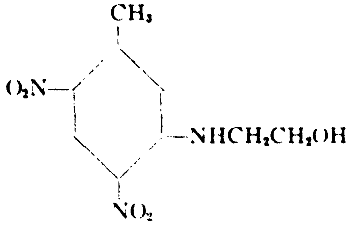
[119] H. R. Fife, U. S. P. 2,053,708, Sept. 8, 1936, to Union Carbide and Carbon Corp.; *Chem. Abs.*, 1936, **30**, 7123.

[120] J. G. Aston, T. E. Peterson and J. Holowchak, *J.A.C.S.*, 1934, **56**, 153; *Chem. Abs.*, 1934, **28**, 1703; *Brit. Chem. Abs.* A, 1934, 306.

[121] H. Wenker, *J.A.C.S.*, 1935, **57**, 2328; *Chem. Abs.*, 1936, **30**, 79; *Brit. Chem. Abs.* A, 1936, 194.

under pressure) of higher homologues of ethylene oxide with a (β,γ-dihydroxypropyl)- or a (γ-alkoxy-β-hydroxypropyl)-aminobenzene.[128]

Monoethanolamine reacts with 2,4,5-trinitrotoluene to form a substitution product, 4,6-dinitro-3-ethyloltoluidine, m.p. 115°C., one nitro group being eliminated from the aromatic nucleus during reaction. On the other hand, di- and triethanolamines do not undergo a similar condensation but yield addition compounds with trinitrotoluene.[129]



Under the influence of heat any one of the ethanolamines may function as a reducing agent, the reaction being said to depend on the decomposition of the amino-alcohol into ammonia and an aldehyde. The reduction of anthraquinone, azobenzene and acetone to anthranol, aniline and isopropyl alcohol, respectively, under the influence of ethanolamines has been studied by Meltsner, Wohlberg and Kleiner.[130] It was found that the ethanolamines would also reduce aqueous solutions of certain metallic salts, e.g., those of silver, lead and mercury.

The hydroxyl group, or groups, in the ethanolamines may be replaced by chlorine on reaction with thionyl chloride. The method has been employed by Ward[131] for the preparation of the derived chloroethylamines. It was found that the chlorine atoms in these compounds were highly reactive and that β,β',β''-trichlorotriethylamine exhibited a powerful vesicant action as did its hydrochloride. The corresponding primary and secondary compounds had no such action.

Reaction with Inorganic Salts. The ethanolamines are sharply differentiated in their reactions with certain inorganic salts.[132] All will react with cobalt chloride (and certain other bivalent metal salts), in absolute ethyl alcohol solution, to furnish simple addition products. But only the tertiary base yields definite compounds in aqueous solution, under which circumstance the primary and secondary bases give rise to indefinite mixtures of hydroxides and basic cobalt salts. This difference in behavior in aqueous solution has been ascribed by Tettamanzi[133] to the lower basicity of triethanolamine as evinced by the lower *p*H values of its 0.1*M* aqueous solutions. Hieber and Levy[134] have described a large number of double compounds of mono-, di- and triethanolamine with cobalt, nickel, copper and zinc salts.

In the reaction between triethanolamine and metallic salts in aqueous solution, several different types of combination have been found to occur. The interaction of triethanolamine with aqueous salts of nickel, cadmium, calcium, strontium and magnesium was found by Tettamanzi and Carli[135] to result in the formation of double compounds of the type $MCl_2 \cdot 2$(triethanolamine), in which the metal is probably coordinated through the oxygen of the hydroxyl groups or the nitrogen atoms. On the other hand, the effect of triethanolamine on aqueous solutions of cobalt chloride, cobalt bromide, cobalt thiocyanate, copper thiocyanate, zinc chloride, zinc sulphate and cadmium chloride has been found by Garelli and Tettamanzi[136] to involve double decomposition with the formation of mixed halide alcoholates in which one or more metal atoms replace the hydrogen atoms of the hydroxyl groups of the tertiary base. This type of reaction is exemplified by the combination of hydrated triethanolamine with cobalt chloride according to the equations:

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[128] British P. 442,024, 1936, to I. G. Farbenind A.-G.; *Chem. Abs.*, 1936, **30** 4512. Addition to British P. 409,237 and 409,238, 1934; *Chem. Abs.*, 1934, **28**, 6322

[129] G. Racciu, *Atti accad. sci. Torino, Classe sci. fis., mat. nat.*, 1934, **69**, 364; *Chem. Abs.*, 1935, **29**, 6217; *Brit. Chem. Abs.* **A**, 1935, 613.

[130] M. Meltsner, C. Wohlberg and M. J. Kleiner, *J.A.C.S.*, 1935, **57**, 2554; *Chem. Abs.*, 1936, **30**, 1741; *Brit. Chem. Abs.* **A**, 1936, 319.

[131] K. Ward, Jr., *J.A.C.S.*, 1935, **57**, 914; *Brit. Chem. Abs.* **A**, 1935, 849; *Chem. Abs.*, 1935, **29**, 4328.

[132] E. Jaffe (*Industria chimica*, 1934, **9**, 750; *Brit. Chem. Abs.* **A**, 1934, 875; *Chem. Abs.*, 1934, **28**, 6652) describes some reactions of triethanolamine with certain inorganic compounds in aqueous solution. *Cf.* A. Tettamanzi and B. Carli, *Gazz. chim. ital.*, 1933, **63**, 566; *Chem. Abs.*, 1934, **28**, 1295; *Brit. Chem. Abs.* **A**, 1933, 1280.

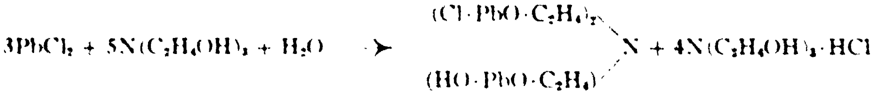
[133] A. Tettamanzi, *Atti accad. sci. Torino, Classe sci. fis., mat. nat.*, 1934, **69**, 369; *Chem. Abs.*, 1935, **29**, 6164; *Chem. Zentr.*, 1935, I, 190; *Brit. Chem. Abs.* **A**, 1935, 849.

[134] W. Hieber and E. Levy, *Z. anorg. Chem.*, 1934, **219**, 225; *Brit. Chem. Abs.* **A**, 1934, **1187**; *Chem. Abs.*, 1935, **29**, 118.

$$(HOCH_2CH_2)_3N + H_2O + CoCl_2 \longrightarrow Co(OH)Cl + (HOCH_2CH_2)_3NHCl$$
$$Co(OH)Cl + (HOCH_2CH_2)_3N \longrightarrow ClCoOC_2H_4N(CH_2CH_2OH)_2 + H_2O$$

Similar compounds, in which the triethanolamine behaves as an ammonium base, have been obtained with certain salts of beryllium and lead and also with nickel iodide. Further studies of these complexes of triethanolamine with aqueous solutions of metallic salts have been contributed by Garelli[137] and by Tettamanzi and Carli.[138]

Garelli[139] also studied the combinations occurring on addition of triethanolamine to concentrated solutions of metallic salts in water. In case of nickel, calcium, strontium and magnesium chlorides, double salts resulted, taking the form of colored crystals, e.g., $CaCl_2 \cdot 2N(C_2H_4OH)_3$. Similar compounds were obtained with nickel bromide and nitrate, cobalt iodide, lead acetate and the sulphates of nickel, cadmium and copper. On the other hand, with lead chloride and some other salts, hydrogen atoms of the hydroxyl groups were substituted, as may be indicated in the reaction



$$3PbCl_2 + 5N(C_2H_4OH)_3 + H_2O \longrightarrow \begin{matrix} (Cl \cdot PbO \cdot C_2H_4)_2 \\ \\ (HO \cdot PbO \cdot C_2H_4) \end{matrix} \!\!> N + 4N(C_2H_4OH)_3 \cdot HCl$$

In this connection, it is interesting to note that Brockman and Nowlen[140] have obtained good electrodeposition of both nickel and cobalt from solutions of these metals containing either an excess of triethanolamine or just enough to give a clear solution. From similar solutions of cobalt sulphate-triethanolamine it was also possible to plate the metal successfully on copper, steel, nickel and zinc with cathode efficiencies as high as 98 per cent. Alloys of nickel and cobalt have also been deposited from triethanolamine solutions of these metals.[141] They contained nickel chloride and sulphate, cobalt sulphate and some sodium sulphate. The concentrations of nickel and cobalt may vary over a wide range; the current densities ran from 3.4 to 15.5 amperes per square decimeter.

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[135] A. Tettamanzi and B. Carli, *Gazz. chim. ital.*, 1933, **63**, 566; *Chem. Abs.*, 1934, **28**, 1295; *Brit. Chem. Abs.* **A**, 1933, 1280.

[136] F. Garelli and A. Tettamanzi, *Gazz. chim. ital.*, 1933, **63**, 570; *Chem. Abs.*, 1934, **28**, 1295; *Brit. Chem. Abs.* **A**, 1933, 1280. Also F. Garelli and A. Tettamanzi, *Atti accad. sc. Torino, Classe sci. fis., mat. nat.*, 1934, **69**, 89; *Chem. Abs.*, 1935, **29**, 5766; *Brit. Chem. Abs.* **A**, 1934, 1208.

[137] F. Garelli, *Atti accad. sci. Torino, Classe sci. fis., mat. nat.*, 1933, **68**, 398, *Chem. Abs.*, 1934, **28**, 2638.

[138] A. Tettamanzi and B. Carli, *Gazz. chim. ital.*, 1934, **64**, 315; *Chem. Abs.*, 1934, **28**, 5360; *Brit. Chem. Abs.* **A**, 1934, 993.

[139] F. Garelli, *IX Congr. intern. quim. pura aplicada, Madrid*, 1934, **3**, 295; *Chem. Abs.*, 1936, **30**, 4114.

[140] C. J. Brockman and J. P. Nowlen, *Trans. Electrochem. Soc.*, 1936, **69**, 45; *Chem. Abs.*, 1936, **30**, 966; *Brit. Chem. Abs.* **B**, 1936, 458.

[141] C. J. Brockman and J. P. Nowlen, *Trans. Electrochem. Soc.*, 1936, **69**, 349; *Chem. Abs.*, 1936, **30**, 3332; *Brit. Chem. Abs.* **B**, 1936, 551.

Double compounds of triethanolamine with calcium chloride, iodide and bromide and also with sodium iodide, potassium iodide and lithium chloride as well as a compound of diethanolamine with calcium bromide have been reported[142] for use in the dissolution of acid products, such as barbituric acids, in aqueous media.

Raymond[143] has observed that, whereas both nickel and cobalt form soluble complex compounds with triethanolamine in the presence of excess aqueous caustic soda, the nickel complex is quantitatively decomposed on boiling, that of cobalt being stable. A quantitative separation of nickel from cobalt, by precipitation of nickel hydroxide, is said to be possible by this procedure.

When an ammoniacal aqueous solution of nickel sulphate is added to a solution of triethanolamine containing caustic potash, a green color is obtained even in the presence of 1 part per 5000 of triethanolamine. This coloration is said by Jaffe[144] to be specific and to be capable of use in the colorimetric estimation of either nickel or triethanolamine. According to Simon,[145] the formation of a purple coloration when solutions of triethanolamine (made alkaline with ammonia) are treated with cobalt chloride, is not sufficiently characteristic or sensitive for the detection of the tri-amine in toilet preparations.

For the determination of triethanolamine in toilet creams and emulsions, Fleck[146] precipitates it as the hydroiodide, $(CH_2OHCH_2)_3N \cdot HI$, m.p. 169°C., which contains 53.6 per cent of the base. On weighing the compound after washing with isopropyl alcohol, a correction is applied for the slight solubility of this addition compound, namely, 1 mg. per ml. of alcohol used. Florentin and Ruiz[147] suggest that the amine can be identified by the microscopical characteristics of its chloroaurate, chloroplatinate and best of all its silicotungstate. The formula of the latter is $SiO_2\,12WO_2 \cdot 4N(C_2H_4OH)_3$. The chlorometallic salts are soluble in water but may be crystallized from alcohol. The tungstate is a precipitate soluble in excess of the reagent.

Quaternary ammonium compounds of the type $N(R\ OH)_4$, are produced by the action of alkene oxides on tertiary alkylolamines, if the alkalinity of the mixture is maintained almost at the neutral point at the beginning of the treatment.[148] Hydrogen chloride, formic, acetic, lactic or stearic acids, or mono sodium phosphate have been found suitable for buffering the solution in this manner, but carbon dioxide is not effective. For example, when a soap made from stearic acid and triethanolamine is treated with ethylene oxide, the foaming agent obtained may be converted into tetraethanol ammonium hydroxide by reaction with sodium hydroxide solution. Or, if a solution of the same tri-amine in aqueous sulphuric acid has been treated successively with ethylene oxide and mineral acid, the product will furnish the quaternary compound on addition of barium hydroxide.

The salts of the quaternary alkylolammonium compounds are soluble in 35 per cent sodium hydroxide solution. They include such compositions as tetra-(β-hydroxyethyl)-ammonium hydroxide, acetate, stearate, disodium phosphate, tri-(β-hydroxyethyl)-butyl and diethyl-di(β-hydroxyethyl)-ammonium hydroxide.

[142] British P. 436,008, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1935, 1165.

[143] E. Raymond, *Compt. rend.*, 1935, 200, 1850; *Brit. Chem. Abs.* A, 1935, 951; *Chem. Abs.*, 1935, 29, 5038.

[144] E. Jaffe, *Industria chimica*, 1934, 9, 151; *Chem. Abs.*, 1934, 28, 4336; *Brit. Chem. Abs.* A, 1934, 396.

[145] W. E. Simon, *Pharm.-Ztg.*, 1934, 79, 842; *Brit. Chem. Abs.* B, 1934, 823; *Chem. Abs.*, 1935, 29, 3462.

[146] H. R. Fleck, *Analyst*, 1935, 60, 77; *Chem. Abs.*, 1935, 29, 2478; *Brit. Chem. Abs.* B, 1935 347.

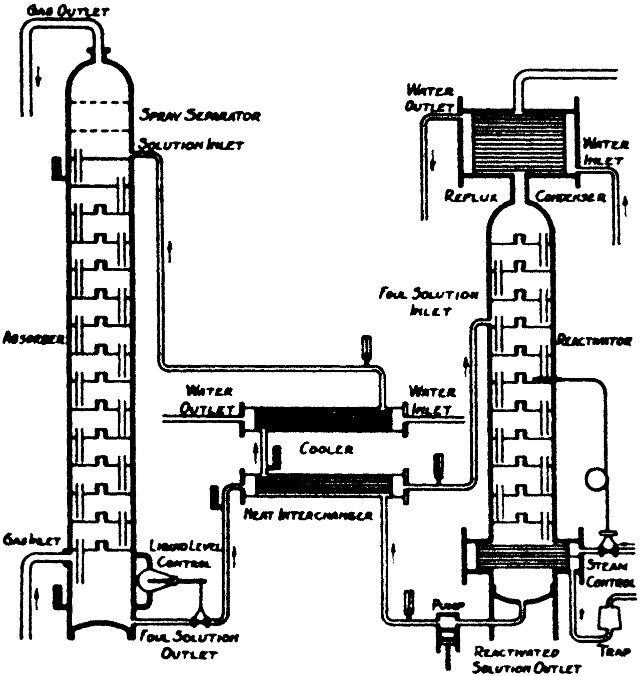
[147] D. Florentin and I. Ruiz, *Ann. fals.*, 1936, 29, 197; *Chem. Abs.*, 1936, 30, 4788; *Brit. Chem. Abs.* A, 1936, 828.

[148] British P. 448,251, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, 30, 7255; *Brit. Chem. Abs.* B, 1936, 780.

USES OF THE ETHANOLAMINES

The ethanolamines and particularly triethanolamine are finding increasing application in the industries. Among the numerous chemical products made from ethylene oxide, these amines must be classed as subsidiary only to the glycol ethers in technical importance.

The ethanolamines, especially the tri- and di- forms, are employed in the removal of carbon dioxide and hydrogen sulphide from gases. The operation is usually carried out in countercurrent operations and sometimes under pressure. The dissolved gases are readily removed from the absorption liquid by heating. Developments in the so-called Girbotol purification system, in which ethanolamines are employed, have been reviewed by Bottoms and Wood.[149] According to Allner,[150] a 50 per cent aqueous solution of triethanolamine is about equal, as regards its performance in carbon dioxide removal, to a 20 per cent potassium carbonate solution. Although the dissolved amine does not tend to deposit crystals, its use necessitates very careful packing of pump glands if leakage is to be avoided. Hirst and Pinkel[150a] state that a 50 per cent aqueous solution of triethanolamine is



Courtesy Girdler Corp.
Courtesy Industrial and Engineering Chemistry

FIG. 137.—Apparatus for Removal of Carbon Dioxide and Hydrogen Sulphide from Gases by Absorption with Ethanolamines. (R. R. Bottoms)

less efficient than either a 50 per cent solution of diethanolamine or a 5 per cent solution of tetramine. In ethanolamine solutions for gas purification, Bottoms[151] proposes to include boric acid for inhibiting corrosion of the apparatus. He also points out[151a] that such corrosion of iron or steel and decomposition of the ethanolamine may be prevented by means of vanadium or arsenic compounds, such as sodium arsenite or vanadate. Removal of carbon dioxide by countercurrent scrubbing with triethanolamine bicarbonate solution under pressure, followed by regeneration by heating under reduced pressure, has been described by Allen and Michalske.[152]

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[149] R. R. Bottoms and W. R. Wood, *Refiner*, 1935, **14**, 105; *J. Inst. Pet. Tech.*, 1935, **21**, 169A; *Chem. Abs.*, 1935, **29**, 7108. See also German P. 606,162, 1934; *Chem. Abs.*, 1935, **29**, 1288. French P. 746,205, 1933; *Chem. Abs.*, 1933, **27**, 4324.

[150] W. Allner, *Chem. Fabr.*, 1935, **8**, 344; *Brit. Chem. Abs.* B, 1935, 979; *Chem. Abs.*, 1935, **29**, 7616.

[150a] L. L. Hirst and I. I. Pinkel, *Ind. Eng. Chem.*, 1936, **28**, 1313; *Brit. Chem. Abs.* B, 1937, 35.

Comparisons of absorption of carbon dioxide by aqueous solutions of tri- and monoethanolamines and of diaminopropanol, $(NH_2CH_2)_2CHOH$, have been made by Gregory and Scharmann.[152a] They found that triethanolamine was only about one-half as effective as monoethanolamine or the diamino compound. The heat of absorption of carbon dioxide in both of the two latter substances was high, about 750 B.t.u. per lb. of dioxide, thus necessitating the use of dilute solutions (about 30 per cent) of the absorbents. It was also noted that in all instances the liquids must be kept free of dissolved oxygen otherwise they exert considerable corrosive action on the apparatus employed.

Fife[153] eliminates sulphur compounds from industrial gases by scrubbing with water containing 15-30 per cent of ethanolamines and not less than 1 per cent of a soluble compound of copper, iron, nickel or zinc. The solution is regenerated by aeration followed by addition of unslaked lime. The foaming tendency of such aqueous solutions is said to be suppressed by continuously circulating a portion of the solution through activated carbon. A small proportion of fatty oil may also be added to the solution with advantage. An ethanolamine, such as monoethanolamine, containing 3 per cent of boric acid, has been proposed[154] as a component of absorption liquids for weak gaseous acids, and a solution of triethanolamine is specifically recommended[155] for the removal of hydrogen sulphide from gases. A number of complex bases, including those with at least 2 nitrogen atoms and at least one hydroxyalkyl or hydroxyaryl group, have also been suggested for this purpose.[156] Brachfeld and Smola[157] propose to remove carbon dioxide, but not hydrogen sulphide, from gases by washing with an undiluted difficultly volatile amine, such as ethanolamines and morpholine derivatives. The absorbed gases may be recovered by treatment at raised temperatures with the vapor of a water-insoluble organic solvent, such as benzene, which forms an azeotropic mixture with water.

Govers[158] reports that after distillation of a petroleum fraction (under reduced pressure) in the presence of a gaseous distillant, e.g., sulphur dioxide or carbon dioxide, the latter may be removed from the liquid by treatment with the tri-amine.

In another method,[159] a gaseous mixture containing ammonia and hydrogen

For the equilibrium absorption of carbon dioxide by ethanolamines, see J. W. Mason and B. F. Dodge, *Trans. Am. Inst. Chem. Engrs.*, 1936, **32**, 27.

[151] R. R. Bottoms, U. S. P. 1,964,808, July 3, 1934, to The Girdler Corp.; *Brit. Chem. Abs.* **B**, 1935, 992; *Chem. Abs.*, 1934, **28**, 5186. *Cf.* U. S. P. 2,065,112, Dec. 22, 1936; *Chem. Abs.*, 1937, **31**, 845.

[151a] R. R. Bottoms, U. S. P. 2,031,632, Feb. 25, 1936, to The Girdler Corp.; *Chem. Abs.*, 1936, **30**, 2283.

[152] A. S. Allen and A. Michalske, U. S. P. 1,934,472, Nov. 7, 1933; *Brit. Chem. Abs.* **B**, 1934, 717; *Chem. Abs.*, 1934, **28**, 616.

[152a] L. B. Gregory and W. B. Scharmann, *Ind. Eng. Chem.*, 1937, **29**, 514.

[153] H. R. Fife, U. S. P. 1,989,004, Jan. 22, 1935, to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1935, 1077; *Chem. Abs.*, 1935, **29**, 1903.

[154] British P. 427,394 and 428,059, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1935, 793; *J. Inst. Pet. Tech.*, 1935, **21**, 266A; *Chem. Abs.*, 1935, **29**, 6111.

[155] French P. 761,060, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 4211.

[156] French P. 785,276, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 600.

[157] J. A. Brachfeld and A. Smola, Austrian P. 135,047, 1933; *Chem. Abs.*, 1934, **28**, 841.

[158] F. X. Govers, U. S. P. 1,959,714, May 22, 1934, to Indian Refining Co.; *Chem. Abs.*, 1934, **28**, 4592; *Brit. Chem. Abs.* **B**, 1935, 290.

[159] French P. 778,182, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 4553.

sulphide is first washed with sulphuric acid to form ammonium sulphate. Monoethanolamine in aqueous solution is then utilized for removal of the sulphide. The latter is recovered by heating the solution and is converted into sulphur dioxide and then progressively to sulphuric acid.

SOAPS

The ethanolamines may be employed in the form of their soaps, the aqueous solutions of which have low surface and interfacial tensions and hence exhibit good emulsifying properties. Triethanolamine ȯleate is, perhaps, the most commonly used. On account of its solubility in organic solvents it finds application in dry cleaning.[160] One composition of this type consists of a paste of the soap in an alcohol (e.g., n-propyl) admixed with a hydroxy ether (for example, the butyl ether of ethylene glycol), water and a low-boiling petroleum distillate.[161] Another method of preparing alcohol amine soaps has been described.[161a] It consists of partially sulphonating petroleum oil with sulphuric acid, separating the acid sludge, and admixing the remaining acid oil with triethanolamine.

The use of alkylolamines in the fat, oil and wax industries has been reviewed by Fischer.[162] Triethanolamine soaps have been proposed as constituents of lip-rouge,[163] in cosmetic preparations with glycol derivatives,[164] in products for glazing or finishing textile materials,[165] in the separation of wax from oils,[165a] and in the oil-proofing of porous fibrous material.[166] Hydroxyalkylamines, such as diethanolamine, are recommended as ingredients of an aqueous bath for use in washing and cleansing textiles, cotton and wool.[167] Salts of ethanolamines with oleic, ricinoleic and stearic acids, have been suggested as dispersing and emulsifying agents, soluble oils and antiseptics,[168] and as antiknock ingredients for motor fuels.[169] Naphthenic sulphonic acid salts of the alkylolamines are proposed as auxiliary agents in hydraulic cement.[170]

The products of the reaction ȯf carboxylic acids (particularly of more than 10 carbon atoms) with alkylolamines are proposed by Ellis[171] for increasing the load-bearing capacity of mineral lubricating oils. Addition is made to the extent of about 0.5 per cent or more. Such compounds include both esters and salts of alkylolamines, preferably the trihydroxyamines such as triethanolamine. Beale[172] recommends an alkylolamine salt of a fatty acid as a top cylinder lubricant. It is

[160] See for example, *Ind. Chem*., 1934, **10**, 149; *Chem. Abs.*, 1934, **28**, 1211; *J. Inst. Pet. Tech.*, 1934, **20**, 469A.

[161] D. R. Merrill, U. S. P. 2,052,881, Sept. 1, 1936, to Union Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 7362.

[161a] K. T. Steik, U. S. P. 2,061,601, Nov. 24, 1936, to Standard Oil Development Co; *Chem. Abs.*, 1937, **31**, 843.

[162] E. J. Fischer, *Allgem. Oel- u. Fett-Ztg*., 1935, **32**, 489; *Brit. Chem. Abs.* **B**, 1936, 159; *Chem. Abs.*, 1936, **30**, 1599.

[163] S. Sabetay, French P. 786,828, 1935; *Chem. Abs.*, 1936, **30**, 822.

[164] N. D. Harvey, Jr., U. S. P. 1,979,385, Nov. 6, 1934, to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1935, 924; *Chem. Abs.*, 1935, **29**, 296. French P. 798,506, 1936, to Soc. anon Tokalon; *Chem. Abs.*, 1936, **30**, 7286.

[165] E. E. Pendlebury, British P. 431,275, 1934; *Brit. Chem. Abs.* **B**, 1935, 800, *Chem. Abs.*, 1936, **30**, 320.

[165a] J. A. Anderson, U. S. P. 2,059,837, Nov. 3, 1936, to Standard Oil Co of Ind; *Chem. Abs.*, 1937, **31**, 535; *J. Inst. Pet. Tech.*, 1937, **23**, 69A.

[166] B. Clayton, British P. 425,986, 1935; *Brit. Chem. Abs.* **B**, 1935, 511; *J. Inst. Pet. Tech.*, 1935, **21**, 223A; *Chem. Abs.*, 1935, **29**, 5675.

[167] H. Ulrich and G. Schuster, U. S. P. 1,935,217, Nov. 14, 1933, to General Aniline Works; *Chem. Abs.*, 1934, **28**, 914.

[168] J. G. Kern and C. J. Sala, U. S. P. 1,946,079 and 1,946,080, Feb. 6, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 2365; *Brit. Chem. Abs.* **B**, 1934, 1003.

[169] French P. 793,967, 1936, to "Les savons nouveaux" compagnie Sapoflor; *Chem. Abs.*, 1936, **30**, 4662.

[170] G. R. Tucker, U. S. P. 2,052,586, Sept. 1, 1936; *Chem. Abs.*, 1936, **30**, 7126.

[171] Carleton Ellis, U. S. P. 2,018,758, Oct. 29, 1935, to Standard Development Co.; *Chem. Abs.*, 1936, **30**, 282; *Brit. Chem. Abs.* **B**, 1936, 1080.

[172] E. B. Beale, U. S. P. 1,990,365, Feb. 5, 1935, to Standard Oil Co. of Indiana; *Chem. Abs.*, 1935, **29**, 1979; *Brit. Chem. Abs.* **B**, 1936, 9.

added in the proportion of 20 to 200 cc. per gallon of gasoline. The salt may be first dissolved in a mineral oil and added to the fuel or mechanically introduced into the cylinder.

The esters of hydroxyamines with higher carboxylic, sulphonic or sulphocarboxylic acids are suggested as dispersing agents for graphite in lubricant manufacture. The monooleic ester of triethanolamine is typical of the suggested substances.[173] Stable emulsions may be obtained from triethanolamine, oleic acid and kerosene and other mineral oils or sulphonic derivatives of petroleum.[174] The physical characteristics of such emulsions have been studied by Risi and Bernard,[175] who also compared their lubricating properties with those of technical lubricants. Another composition which may be employed as a lubricant comprises hydrogenated mineral oil emulsified with water, employing ethanolamine as the dispersing agent.[176]

The phosphoric acid salts of esterified alkylolamines are utilized by Albrecht[177] as constituents of rust-preventive or coating compositions. Thus, triethanolamine is esterified by heating at 176-250°C. with a higher fatty or resin acid of molecular weight greater than 150, for example, the acids of linseed oil. The resulting ester is then converted into its orthophosphate. The products are soluble in paint and varnish media and have rust-preventing properties when applied to metal surfaces.[178] Small quantities of citric or tartaric acids are added to counteract an "alligatoring" effect in the film.

Shaving compositions are said to be improved by the incorporation of 15-30 per cent (calculated on the soap and other solids present) of a secondary or tertiary phosphate of an organic base, such as triethanolamine. Combinations of mono- or polyhydric alcohol-amines with mineral or organic acids, other than those forming soaps, are proposed by Coustolle[179] as ingredients in cleansing agents for the skin. The proposed acids include hydrochloric, sulphuric, nitric, phosphoric, boric and glycerophosphoric. Dispersing agents advanced by Bertsch[180] consist of the reaction product of aliphatic hydroxyamines and sulphonated high-molecular weight aliphatic alcohols of more than 8 carbon atoms, for example, the triethanolamine salt of the sulphuric acid ester of oleyl alcohol.

Triethanolamine has been suggested as a useful addition to a wide variety of products (some which have been noted) including dentrifices,[181] shaving cream and soap,[182] hair dyes,[183] soldering flux,[184] lime-soap greases,[185] foundry sand-core compositions,[186] aluminum soap to be used with gasoline or benzene for waterproofing fabrics or stone[187] and as a component of a material for the manufacture of gaskets.[188] Other suggested applications of this trialkylolamine are in aniline black printing,[189] in the manufacture of rubber sponge,[190] in the preparation of sizing, proofing, wetting and scouring agents for textiles,[191] in the removal of "catalyst taste" of hydrogenated oils[192] and for refining the oils obtained by separation of oil-water emulsions.[193] A solid wax dispersion, used in the preparation of emulsions for coating citrus fruits,[194] may be made of paraffin and carnauba waxes, cottonseed oil, oleic acid and triethanolamine (10 per cent by weight).

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[173] A. Bauer and U. Ehrhardt. German P. 612,015 1935, to I. G. Farbenind A.-G.; *Chem. Abs.*, 1935, **29**, 4934. J. W. Orelup, British P. 450,672, 1936; *J. Inst Pet Tech.*, 1936, **22**, 465A.

[174] British P. 446,314, 1936, to Standard Oil Development Co; *Chem. Abs.*, 1936, **30**, 6853.

[175] J. Risi and H. Bernard, *Can J. Research*, 1934, 11, 247; *Brit Chem Abs.* **B**, 1934, 949; *Chem. Abs.*, 1934, **28**, 7508

[176] French P. 789,626, 1935, to International Hydrogenation Patents Co., Ltd.; *Chem. Abs.*, 1936, **30**, 1989.

[177] H. O. Albrecht, U. S. P 1,936,534, Nov. 21, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1934, 805; *Chem Abs*, 1934, **28**, 736 British P. 407,008, 1932; *Brit. Chem. Abs.* **B**, 1934, 413.

[178] H. O. Albrecht, U. S. P. 1,936,533, Nov. 21, 1933, to E. I. du Pont de Nemours & Co; *Brit. Chem. Abs.* **B**, 1934, 825.

[179] P. P. Coustolle, French P. 784,404, 1935; *Chem. Abs*, 1936, **30**, 250.

[180] H. Bertsch, German P. 622,640, 1935, to Böhme Fettchemie G.m.b.H.; *Chem. Abs.*, 1936, **30**, 3548.

[181] C. C. Vogt, U. S. P. 1,969,340, Aug. 7, 1934; *Brit. Chem. Abs.* **B**, 1935, 656; *Chem. Abs.*, 1934, **28**, 6252.

[182] L. Szigethy, Hungarian P. 111,897, 1935; *Chem. Abs.*, 1935, **29**, 3869.

[183] E. Basch, German P. 582,521, 1933; *Chem. Abs*, 1934, **28**, 860.

[184] H. S. McQuaid, U. S. P. 1,949,916, Mar. 6, 1934, to Grasselli Chemical Co.; *Brit. Chem. Abs.* **B**, 1935, 315; *Chem. Abs.*, 1934, **28**, 3050.

[185] W. D. Hodson, U. S. P. 1,982,662, Dec. 4, 1934; *Brit Chem. Abs.* **B**, 1936, 335; *Chem. Abs.*, 1935, **29**, 629.

[186] H. L. Quandt and J. J. Horak, U. S. P. 2,004,344, June 11, 1935, to Quandt Chemical Co.; *Brit. Chem. Abs.* **B**, 1936, 358; *Chem. Abs.*, 1935, **29**, 4727.

Free alkylolamines may be recovered from extracts or residues obtained in refining oils, fats, waxes and resins.[195] The method recommended consists of distillation with steam under reduced pressure after the addition of basic substances such as alkali soaps or alkali or alkaline-earth oxides to suppress amide formation. The low-boiling fractions contain alkyl- and alkylolamines. Kaladzhal[196] found that the influence of aluminum stearate in lowering the pour point of mineral lubricating oils is enhanced by the addition of small proportions of triethanolamine. An anti-rusting composition for preventing corrosion in stored engines may be prepared[197] from 5 to 6 per cent of triethanolamine, 10 per cent aluminum stearate, 10 to 12 per cent butanol and lard oil.

Triethanolamine (and similar bases) have been recommended for use in the preservation and stabilization of a number of organic chemicals. Thus, glycol ethers which tend to deteriorate on storage are preserved against discoloration by the addition of less than 1 per cent, generally about 0.1 per cent by volume, of the base.[198] Aromatic alcohols, such as benzyl alcohol, prepared from the corresponding halide by hydrolysis, are said[199] to be stabilized by heating with about 3 per cent of a high-boiling base, such as triethanolamine, at above 100°C., followed by distillation. The addition of not more than 0.02 per cent of an ethanolamine to petroleum distillates, such as gasolines or kerosenes, is purported[200] to render them stable as regards color, gum formation and odor.

Alkylolamines are suggested[201] as agents for increasing the heat resistance and for diminishing any corrosive action of cellulose esters and ethers. They may also be applied in the refining of the esters.[202] Neutral solutions of inorganic salts of such bases, particularly of triethanolamine, are employed to effect fireproofing of textile materials without affecting the pliability and smoothness necessary for subsequent processing operations.[203] Triethanolamine lactate is proposed[204] as an agent for the treatment of filaments, films and fabrics. Rayon is said to be protected from the injurious action of oxidation products of drying oils by inclusion, in the dressing, of a water-soluble base such as triethanolamine.[205] The ethanolamines and related compounds have found application in such varied uses as the concentration of aliphatic acids,[206] the reclaiming of oils containing carbon,[207] the inhibition of corrosion in automobile radiators,[207a] and the manufacture of esters of leuco-compounds of vat dyes.[208]

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[187] J. Dolid, U. S. P. 2,032,528, Mar. 3, 1936; *Chem. Abs.*, 1936, **30**, 2775.

[188] H. H. Jordan, U. S. P. 1,941,437, Dec. 26, 1933, to Armstrong Cork Co.; *Chem. Abs.*, 1934, **28**, 1488; *Brit. Chem. Abs.* **B**, 1935, 111.

[189] R. Haller, U. S. P. 1,952,247, Mar. 27, 1934, to Soc. pour l'ind. chim. à Bale; *Chem. Abs.*, 1934, **28**, 3596.

[190] R. R. Olin, U. S. P. 1,912,591, June 6, 1933, to C. P. Hall; *Brit. Chem. Abs.* **B**, 1934, 159, *Chem. Abs.*, 1933, **27**, 4440.

[191] F. J. Moseley, British P. 401,282, 1932; *Brit. Chem. Abs.* **B**, 1934, 136; *Chem. Abs.*, 1934, **28**, 2433. French P. 749,446, 1933; *Chem. Abs.*, 1934, **28**, 546.

[192] D. Hildisch, U. S. P. 2,021,552, Nov. 19, 1935; *Chem. Abs.*, 1936, **30**, 637.

[193] M. De Groote, B. Keiser and A. F. Wirtel, U. S. P. 2,034,941, Mar. 24, 1936, and 2,023,993, Dec. 10, 1935, to Tretolite Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 200A; *Chem. Abs.*, 1936, **30**, 1218, 3215.

[194] J. R. MacRill, U. S. P. 2,019,758, Nov. 5, 1935, to California Fruit Growers Exchange; *Brit. Chem. Abs.* **B**, 1936, 779; *Chem. Abs.*, 1936, **30**, 533. *Cf.* H. Bennett, U. S. P. 1,981,608, Nov. 20, 1934; *Chem. Abs.*, 1935, **29**, 529. British P. 420,760, 1934; *Chem. Abs.*, 1935, **29**, 3428; *Brit. Chem. Abs.* **B**, 1935, 139.

[195] W. J. Hund and L. Rosenstein, British P. 420,269, 1934; *Brit. Chem. Abs.* **B**, 1935, 109, *Chem. Abs.*, 1935, **29**, 3544. Canadian P. 353,510, 1935; *Chem. Abs.*, 1936, **30**, 2416.

[196] R. Kaladzhal, *Neft. Khoz.*, 1934, **26**, No. 4, 40; *Chem. Abs.*, 1934, **28**, 7507.

[197] See, *Nat. Pet. News*, 1936, **28** (1), 24; *J. Inst. Pet. Tech.*, 1936, **22**, 165A.

[198] H. L. Cox, U. S. P. 2,035,383, Mar. 24, 1936; *Chem. Abs.*, 1936, **30**, 2986. British P. 425,728, 1934; *Brit. Chem. Abs.* **B**, 1935, 487; *Chem. Abs.*, 1935, **29**, 5464; *J. Inst. Pet. Tech.*, 1935, **21**, 223A. French P. 773,450, 1934; *Chem. Abs.*, 1935, **29**, 1430. All patents to Carbide and Carbon Chemicals Corp.

[199] L. P. Kyrides, U. S. P. 1,933,064, Oct. 31, 1933, to Monsanto Chemical Co.; *Brit. Chem. Abs.* **B**, 1934, 874; *Chem. Abs.*, 1934, **28**, 482.

[200] J. B. Rather, L. C. Beard, Jr., and O. M. Reiff, U. S. P. 1,989,528, Jan. 29, 1935, to Socony-Vacuum Oil Co.; *Brit. Chem. Abs.* **B**, 1936, 9; *Chem. Abs.*, 1935, **29**, 1978.

[201] C. Dreyfus and G. Schneider, U. S. P. 1,954,729, Apr. 10, 1934, to Celanese Corp. of America; *Brit. Chem. Abs.* **B**, 1935, 144; *Chem. Abs.*, 1934, **28**, 3899.

[202] H. Dreyfus, British P. 427,559, 1935; *Chem. Abs.*, 1935, **29**, 6055; *Brit. Chem. Abs.* **B**, 1935, 588.

The sulphuric esters of mono- and diethanolamine, and also of similar primary and secondary alkylolamines, may be halogenated to yield compounds capable of liberating free halogen and thus are reported to be useful as bleaching agents.[209] The condensation of ester-type waxes with primary or secondary nitrogen bases, such as ethanolamine, is said[210] to furnish products of value as polishes, textile finishes and in rubber compounding. Salts of ethanolamines with aromatic, aromatic-aliphatic or heterocyclic sulphonic or carboxylic acids, containing iodine substituted in the ring, have been described.[211]

A mixture of Carbitol and an organic acid salt of triethanolamine is advocated as a hydraulic pressure-transmitting fluid.[212] Trialkylolamine may be added to solid carbon dioxide to improve its physical characteristics.[213] Greer[214] proposes to employ, *inter alia*, triethanolamine as a dehydrating medium for drying diethyl ether to less than 0.6 per cent of water, the ether being collected by distillation.

Triethanolamine hydroxyabietate may be produced by treating a gasoline solution of wood rosin with triethanolamine.[215] The salt is soluble in alcohol but is hydrolyzed by hot water. Other alkylolamines react similarly with rosin, and it is believed that such treatment may be useful in the refining of rosin.

DIOXANE AND ITS DERIVATIVES

Dioxane and its homologues may be prepared by the dehydration of the corresponding 1,2-glycols under the influence of sulphuric acid. Steimmig and Hambsch[216] have described a continuous process for the preparation of such compounds from a mixture of homologous 1,2-glycols by heating with concentrated sulphuric acid at the boiling point of the acid liquor. The products are allowed to distil off, and a corresponding amount of glycol is continuously added.

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[203] British P. 437,226, 1934, to British Celanese, Ltd; *Brit. Chem. Abs.* **B**, 1936, 100; *Chem. Abs.*, 1936, **30**, 2407.

[204] W. Whitehead, Canadian P. 353,273, 1935, to C. Dreyfus; *Chem. Abs.*, 1935, **29**, 8185.

[205] T. Koch, U. S. P. 1,984,139, Dec. 11, 1934, to American Enka Corp.; *Chem. Abs.*, 1935, **29**, 942; *Brit. Chem. Abs.* **B**, 1936, 17.

[206] J. A. Brachfeld and A. Smola, Austrian P. 135,002, 1933; *Chem. Abs.*, 1934, **28**, 782.

[207] G. J. Strezynski, U. S. P. 2,030,480, Feb. 11, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 216A; *Chem. Abs.*, 1936, **30**, 2366.

[207a] H. L. Cox, U. S. P. 1,992,689, Feb. 26, 1935, to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.*, **B**, 1936, 1046; *Chem. Abs.*, 1935, **29**, 2503.

[208] J. G. Kern, U. S. P. 1,954,702, Apr. 10, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1934, 183; *Chem. Abs.*, 1934, **28**, 3911.

[209] French P. 777,750, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 4106.

[210] British P. 415,789, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1934, 971; *Chem. Abs.*, 1935, **29**, 950.

[211] French P. 790,674, 1935, to Chemische Fabrik vorm. Sandoz; *Chem. Abs.*, 1936, **30**, 2988.

[212] R. R. Fulton, U. S. P. 1,986,260, Jan. 1, 1935, to Puritan Soap Co.; *Brit. Chem. Abs.* **B**, 1935, 1027; *Chem. Abs.*, 1935, **29**, 1183.

[213] C. L. Jones, U. S. P. 2,020,189, Nov. 5, 1935, to Adico Development Corp.; *Chem. Abs.*, 1936, **30**, 335; *Brit. Chem. Abs.* **B**, 1936, 1092.

[214] P. S. Greer U. S. P. 1,974,069, Sept. 18, 1934, to Carbide & Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1935, 761; *Chem. Abs.*, 1934, **28**, 6727.

[215] J. N. Borglin and L. N. Bent, U. S. P. 2,050,263, Aug. 11, 1936, to Hercules Powder Co.; *Chem. Abs.*, 1936, **30**, 6766.

[216] G. Steimmig and O. Hambsch, U. S. P. 1,939,189, Dec. 12, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1366.

Another mode of synthesis of dioxane involves the catalytic dimerization of ethylene oxide. Passage of ethylene oxide at about 120°C. over a solid alkali bisulphate catalyst is said[217] to yield mainly dioxane, whereas a similar treatment in the presence of an alkali hydroxide furnishes more highly polymerized materials of a waxy consistency. Other acid catalysts, such as aluminum hydrosilicate, may be employed for the same purpose in the presence of a solvent (dioxane or a hydrocarbon, ether or ester) at temperatures up to 150°C. in the liquid or vapor phase and at atmospheric or elevated pressure.[218] In like manner, propene oxide vapor is converted into a dimethyldioxane, b.p. 117°C., in the presence of a solid alkali bisulphate catalyst at about 120°C. More highly polymerized viscous liquid products are obtained under similar conditions in the presence of an alkali hydroxide.[219]

Dreyfus[220] discloses that *p*-dioxane, and its alkyl or other derivatives, may be prepared by the polymerization of the appropriate aldehydes under the influence of substances favoring etherification reactions. Examples of such materials are sulphuric acid, ferric chloride, zinc chloride, hydrogen chloride, benzenesulphonic acid, phosphoric acid, alkali bisulphates or acid phosphates. According to this method, *p*-dioxane is produced from formaldehyde while acetaldehyde furnishes dimethyl-*p*-dioxane.

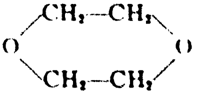
Dreyfus also prepared cyclic ethers by condensation of polyhydric alcohols by means of hydrochloric acid.[221] The alcohol may be dissolved in an inert solvent to serve as a diluent capable of removing the ether in azeotropic mixture. In another process,[222] the glycol or other polyhydric alcohol is used in the form of its alkali or alkaline-earth salt, in which case heating at 160-200°C. in the presence of hydrogen chloride causes dehydration to the corresponding cyclic ether. Here, too, a diluent such as biphenyl is recommended as a means of distilling off the desired product, e.g., dioxane, from ethylene glycol or other di-alcoholate. Further, dioxane may be secured by heating β,β'-dichlorodiethyl ether with copper oxide and lead oxide.[222a]

A method for purifying commercial dioxane involves the removal of low-boiling aldehydes with a volatile inorganic acid.[223] The crude material is distilled with enough water and acid (hydrochloric, hydrobromic or sulphurous) to form a quaternary azeotrope. The undesired aldehyde and the acid pass over quantitatively in the first portions of the distillate. For example, from the following mixture:

96.25 vol. per cent	dioxane (containing 20% aldehyde
0.3 " " "	36% aqueous hydrochloric acid
3.45 " " "	water

all the aldehyde and hydrogen chloride came over at 86-89°C. in the first third of the distillate.

Dioxane has the constitution indicated by the formula



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[217] F. Webel, German P. 597,496, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5080.

[218] German P. 598,952, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 6446

[219] F. Webel, German P. 613,261, addition to 597,496, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 5464.

[220] H. Dreyfus, French P. 772,154, 1934; *Chem. Abs.*, 1935, **29**, 1440.

[221] H. Dreyfus, British P. 408,230, 1934; *Chem. Abs.*, 1934, **28**, 5470; *Brit. Chem. Abs.* **B**, 1934, 492.

[222] H. Dreyfus, British P. 407,035, 1934; *Chem. Abs.*, 1934, **28**, 6444; *Brit. Chem. Abs.* **B**, 1934, 443.

[222a] H. Dreyfus, U. S. P. 2,056,960, Oct. 13, 1936; *Chem. Abs.*, 1936, **30**, 8241.

[223] British P. 442,540, 1934, to Haardt & Co. A.-G.; *Brit. Chem. Abs.* **B**, 1936, 442; *Chem. Abs.*, 1936, **30**, 4518.

It is a neutral, inert, non-hydroxylic liquid of extensive solvent power. It has been recommended by Oxford[224] for use in the determination of molecular weights by the cryoscopic method. However, Roth and Meyer[225] consider the application of dioxane in this connection inadvisable, since its molar freezing point depression, approximately 4.71, was proven inconstant probably because of allotropy. These investigators found the heats of fusion and transition of pure dioxane to be —34.25 and —6.32 g.-cal. per gram, respectively. However, contrary to the general rule, the specific heat of the crystal was greater than that of the liquid.

The melting points, boiling points, refractive indices and densities of binary mixtures of water and dioxane have been determined by Gillis and Delaunois.[226] The melting point data showed a eutectic at —14.82°C., indicating formation of a definite hydrate. The dielectric constants of a series of dioxane-water mixtures between 0° and 80°C. for a wave length of 150 meters have been determined by Åkerlöf and Short.[227] A resonance method previously described by one of the workers was utilized.[227a]

In view of the increasing employment of dioxane as an industrial solvent, the pharmacological properties of the substance are of importance. von Oettingen and Jirouch[228] found that, in common with certain glycol derivatives, dioxane is toxic and possesses a haemolytic action on red blood corpuscles.

It has been shown by Fairley, Linton and Ford-Moore[229] that the *in vitro* final oxidation product of dioxane is oxalic acid with diglycolic acid as a by-product. Formation of these substances is held responsible for tissue injuries.

A detailed examination of the toxic properties of dioxane has been provided by Yant, Schrenk, Waite and Patty,[230] whose main findings may be summarized as follows. Dioxane is much more poisonous than ethylene glycol Exposure to its vapor produces severe irritation of the membranes of eyes and nose. After long exposure, the lungs are affected, narcosis being evident with high concentrations. It was concluded that the low toxicity of dioxane, as compared with carbon tetrachloride or tetrachloroethane, together with warning provided by its irritant nature, make health hazards from breathing its vapors very slight under ordinary conditions of usage and with reasonable exposure. The compound, however, must be deemed hazardous to life in air confined over the liquid in tanks, vats and wherever high concentrations may accumulate.

Dioxane is of interest chemically on account of the ease with which it yields addition compounds of the oxonium type. Thus, Doak[231] noted that with arsenic trichloride it forms a crystalline addition complex of the formula $(C_4H_8O_2)_3 \cdot 2AsCl_3$ (m.p. 62°C.). The latter compound is, however, largely dissociated into its components in benzene or acetone solutions

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[224] A. E. Oxford, *Biochem. J.*, 1934 **28**, 1325; *Chem Abs* 1935 **29**, 1308; *Brit Chem Abs* **A**, 1934, 1087. For the thermal decomposition of dioxane, see P Gross and H Suess, *Monatsh.*, 1936, **68**, 207; *Chem. Abs.*, 1936, **30** 7989; *Brit. Chem. Abs* **A**, 1936, 1208.

[225] W. A. Roth and I. Meyer, *Z Elektrochem.*, 1935, **41**, 229; *Chem Abs* 1935, **29**, 4253; *Brit Chem. Abs.* **A**, 1935, 690.

[226] J. Gillis and A. Delaunois *Rec. trav. chim.*, 1934, **53**, 186; *Chem Abs.* 1935, **29**, 2061, *Brit. Chem. Abs.* **A**, 1934, 357. *See* also F. Hovorka, R A. Schaefer and D. Dreisbach, *J A C S.*, 1936, **58**, 2264; *Chem. Abs.*, 1937, **31**, 935; *Brit. Chem. Abs.* **A** (1), 1937, 23

[227] G. Åkerlöf and O. A. Short, *J.A.C.S.*, 1936, **58**, 1241; *Chem Abs.*, 1936, **30**, 6616.

[227a] G. Åkerlöf, *J.A.C.S.*, 1932, **54**, 4125; *Chem. Abs.*, 1933, **27**, 641; *Brit. Chem Abs* **A**, 1933, 19.

[228] W. F. von Oettingen and E. A. Jirouch, *J. Pharmacol.*, 1931, **42**, 355 See also G. M. Dyson, *Industrial Chemist*, 1934, **10**, 102; *Chem. Abs.*, 1934, **28**, 3131.

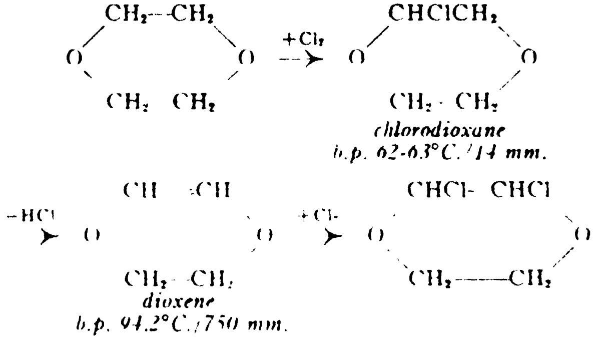
[229] A. Fairley, F. C. Linton and A. H. Ford-Moore, *J. Hyg.*, 1936, **36**, 341; *Chem. Abs.*, 1936, **30**, 7698.

[230] W. P. Yant, H. H. Schrenk, C. P. Waite and F. A Patty, *U. S. Public Health Reports*, 1930, **45**, 2023; *Chem. Abs.*, 1930, **24**, 5071. H. H. Schrenk and W. P. Yant, *J. Ind Hyg. Toxicol.*, 1936, **18**, 448; *Brit. Chem. Abs.* **A**, 1936, 1417. See also W. Wirth and O Klimmer, *Arch. Gewerbepath. Gewerbehyg.*, 1936, **7**, 192; *Chem. Abs.*, 1937, **31**, 775.

[231] G. O. Doak, *J. Am. Pharm. Assoc.*, 1934, **23**, 541; *Chem Abs.*, 1935, **29**, 2539; *Brit. Chem. Abs.* **A**, 1934, 1015.

The products of chlorination of dioxane are the 2,3-dichloro- and a mixture of tetrachloro-derivatives. Kucera and Carpenter[232] found that chlorination in the presence of a little stannous chloride or iodine chloride at 90°C. yields 96.6 per cent of the 2,3-dichloro-compound. The latter could be further chlorinated (without a catalyst) at 145°C. to give an 83-85 per cent yield of a mixture of symmetrical and asymmetrical tetrachloro-compounds.

Summerbell and Bauer[233] consider the chlorination of dioxane to proceed via the monochloro-compound which then decomposes with the elimination of hydrogen chloride to yield dioxene, the complete scheme being:



In support of this mechanism it was observed that chlorodioxane prepared by the direct combination of dioxene with hydrogen chloride was unstable even at room temperature. These investigators have prepared various 2,3-diaryl-substituted dioxanes from the 2,3-dichloro-compound by the Grignard reaction. The 2,3-dihalide can be condensed with ethylene glycol to yield a mixture of two isomeric 2,3-ethylenedioxydioxanes.[234] A later report[235] by the same workers states that better yields of 2,3-dialkyldioxanes are secured if the magnesium alkyl bromide is first treated with an equimolar quantity of anhydrous zinc chloride or cadmium chloride.

Dioxane has been proposed[236] as an inert solvent in the etherification of alkali-cellulose by alkyl or aralkyl halides. Moncrieff and North[237] suggest the use of this liquid as a softening medium in the stretching of non-uniformly hydrolyzed cellulose ester yarns. The reagent is said to have a greater action on the less hydrolyzed portions. It is reported by Young and Perkins[238] that dioxane exerts a preferential solvent action on diolefin hydrocarbons and can thus be employed in the removal of butadiene from butenes and butanes. The separation can be effected by distillation of the hydrocarbon mixture countercurrent to a stream of solvent, the solution recovered being afterwards rectified. Dioxane has been suggested as a solvent for use in the preparation of a coffee extract.[239]

[232] J. J. Kucera and D. C. Carpenter, *J.A.C.S.*, 1935, 57, 2346; *Brit. Chem. Abs.* **A**, 1936, 341; *Chem. Abs.*, 1936, **30**, 1796.

[233] R. K. Summerbell and L. N. Bauer, *J.A.C.S.*, 1935, 57, 2364; *Chem. Abs.*, 1936, **30**, 1795; *Brit. Chem. Abs.* **A**, 1936, 341.

[234] W. Baker and A. Shannon, *J.C.S.*, 1933, 55, 1598; *Chem. Abs.*, 1934, **28**, 1330; *Brit. Chem. Abs.* **A**, 1934, 194.

[235] R. K. Summerbell and L. N. Bauer, *J.A.C.S.*, 1936, 58, 759; *Brit. Chem. Abs.* **A**, 1936, 820; *Chem. Abs.*, 1936, **30**, 4864.

[236] D. C. Ellsworth, U. S. P. 1,980,988, Nov. 20, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 987; *Chem. Abs.*, 1935, **29**, 599.

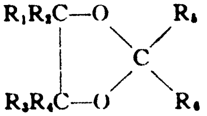
[237] R. W. Moncrieff and C. W. North, British P. 438,119, 1934, to British Celanese, Ltd.; *Brit. Chem. Abs.* **B**, 1936, 96; *Chem. Abs.*, 1936, **30**, 2772.

[238] C. O. Young and G. A. Perkins, U. S. P. 1,948,777, Feb. 27, 1934, to Carbide & Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1935, 12; *Chem. Abs.*, 1935, **29**, 2723.

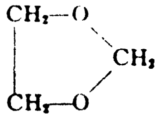
[239] S. Ogura, Japanese P. 110,091, 1935; *Chem. Abs.*, 1935, **29**, 5196.

1,3-DIOXOLANES

The condensation of aldehydes or ketones with 1,2-glycols can be effected in the presence of esterification catalysts[240] to yield cyclic acetals or ketols (1,3-dioxolanes) of the general formula



where R_1, R_2, R_3, R_4, R_5 and R_6 may be alkyl groups or hydrogen atoms. The condensation is carried out by Dreyfus[241] in the presence of a limited amount of water, for example, 1 mole of water for each mole of aldehyde or ketone used. A continuous process for the manufacture of these cyclic products has also been described.[242] Acid sulphates, pyrosulphates or phosphates, especially of the alkali metals, are suggested as catalysts for the reaction. For example, interaction of ethylene glycol and paraformaldehyde may be effected continuously by sodium hydrogen sulphate at 140°C.[243] In this case, the product is 1,3-dioxolane,



This compound is said[244] to be applicable for dissolving cellulose acetates having an acetyl value higher than 56 per cent. The same solvent has been suggested as a medium for the incorporation of plasticizers or other materials into cellulose derivatives, such as the acetate having not less than 56 per cent acetyl value.[245]

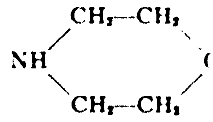
In this connection it is interesting to note that the monoalkyl ethers of glycols may be condensed with formaldehyde by means of ferric chloride or mineral acids as catalysts. The products appear to be straight chain formals of the type

$$ROCH_2CH_2OCH_2OCH_2CH_2OR$$

For example, the addition of formaldehyde to ethylene glycol monomethyl ether gives bis-(β-methoxyethyl)methylene ether, b.p. 197-205°C. They are useful solvents, softeners and plasticizers for cellulose esters such as acetone-soluble cellulose acetate.[246]

MORPHOLINES

The morpholines are a series of cyclic ether amines somewhat closely allied, from the structural point of view, with the dioxanes. Morpholine itself has the constitution indicated by the following formula,



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[240] H. Dreyfus, French P. 745,973, 1933; *Chem. Abs.*, 1933, 27, 4243.

[241] H. Dreyfus, British P. 393,608, 1933; *Brit. Chem. Abs.* B, 1933, 822; *Chem. Abs.*, 1933, 27, 5752. French P. 745,974, 1933; *Chem. Abs.*, 1933, 27, 4243.

[242] H. Dreyfus, British P. 394,678, 1933; *Brit. Chem. Abs.* B, 1933, 856; *Chem. Abs.*, 1933, 27, 5752.

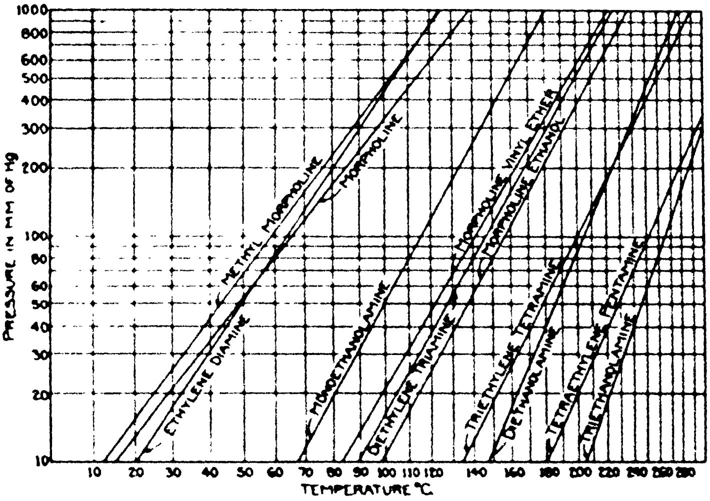
[243] H. Dreyfus, British P. 394,679, 1933; *Brit. Chem. Abs.* B, 1933, 856; *Chem. Abs.*, 1933, 27, 5752.

[244] H. Dreyfus, British P. 407,709, 1932; *Brit. Chem. Abs.* B, 1934, 464.

[245] H. Dreyfus, British P. 397,191, 1931; *Brit. Chem. Abs.* B, 1933, 929.

[246] British P. 424,837, 1933, to British Celanese, Ltd.; *Brit. Chem. Abs.* B, 1935, 619; *Chem. Abs.*, 1935, 29, 5125.

It was first prepared by Knorr[247] who dehydrated diethanolamine with 70 per cent sulphuric acid. In a somewhat analogous manner, Hampton and Pollard[247a] succeeded in securing morpholine in a reported yield of 48 per cent. In this case, diethanolamine was admixed with concentrated hydrochloric acid until the solution was acid to litmus. The mixture was heated to remove water, after which the temperature was raised to 200-210°C. for 15 hours. At the end of that time, the reaction mass was cooled and distilled with calcium oxide. The resulting liquid was dried over solid sodium hydroxide and refluxed with metallic sodium for 30 minutes. Fractionation of the liquid was effected and the portion boiling at 126-129°C. was collected. It may also be derived from β,β'-dihalogenodiethyl ethers by reaction with ammonia or amides.[248] The N-alkyl or aryl-substituted morpholines have been made from β,β'-dichlorodiethyl ether and primary aliphatic or aromatic amines. Thus, N-phenylmorpholine results from heating the halogenated ether with aniline,[249] a similar reaction also occurring in the case of β,β'-dibromodiethyl ether.[250] The condensation of β,β'-dichlorodiethyl ether with phenylhydrazine and other aromatic bases has been investigated by Axe and Freeman.[251]



Courtesy Mellon Institute of Industrial Research
Courtesy Industrial and Engineering Chemistry

FIG. 138.—Vapor Pressures of Various Amines. (A. L. Wilson)

Morpholine is a colorless liquid, b.p. 128.3°C., soluble in all proportions in water. It has a high and varied solvent power and has been suggested as a leveling agent in dye baths[252] and as a general textile assistant for scouring, stripping and boiling-off.[253] By virtue of its basic character, morpholine forms soaps with acids. The oleate and stearate are effective as stabilizers of oil-water emulsions.

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[247] L. Knorr, *Ann.*, 1898, **301**, 1; *J.C.S.*, 1898, **74** (1), 601.

[247a] B. L. Hampton and C. B. Pollard, *J.A.C.S.*, 1936, **58**, 2338; *Chem. Abs.*, 1937, **31**, 408; *Brit. Chem. Abs.* **A** (2), 1937, 36.

[248] J. Sand, *Ber.*, 1901, **34**, 2906; *J.C.S.*, 1901, **80** (1), 741. See also J. B. Payman and H. A. Piggott, U. S. P. 1,859,527, May 24, 1932; *Chem. Abs.*, 1932, **26**, 3808.

[249] O. Kamm and J. H. Waldo, *J.A.C.S.*, 1921, **43**, 2225; *Chem. Abs.*, 1922, **16**, 408.

[250] V. Prelog and V. Stepan, *Collection Czechoslav. Chem. Communications*, 1935, **7**, 93; *Chem. Abs.*, 1935, **29**, 4013; *Brit. Chem. Abs.* **A**, 1935, 629.

[251] W. N. Axe and C. Freeman, *J.A.C.S.*, 1934, **56**, 478; *Brit. Chem. Abs.* **A**, 1934, 536; *Chem. Abs.*, 1934, **28**, 1704.

[252] H. Ulrich and J. Nuesslein, U. S. P. 1,923,243, Aug. 22, 1933; *Chem. Abs.*, 1933, **27**, 5198.

According to Wilson,[254] morpholine was not commercially available as a solvent until 1935. It has a penetrating but not unpleasant odor suggestive of ammonia. It absorbs both moisture and carbon dioxide from the air, forming a carbamate which can be sublimed almost unchanged on heating at 95-100°C. It is water-soluble, cannot be "salted out" though it becomes immiscible with strong solutions of sodium hydroxide. A 95 per cent aqueous morpholine is in equilibrium with a 50 per cent solution of caustic soda.

Combinations of morpholine with many acidic bodies seem to be loosely held, since the amine may be recovered by distillation from its addition products with oleic acid or phenol. Water solutions of its salts with weak gaseous acids give up morpholine on boiling.

The soaps serve especially well in the production of coating emulsions, certain types of films exhibiting water-resistance.

TABLE 122.—*Some Physical Constants of Morpholines.*

Compound and Formula	Specific Gravity 20°/20°C.	Boiling Point (760 mm.) °C.	Vapor Pressure 20°C. mm.
Morpholine, $NH(C_2H_4)_2O$	1.0016	128.3	13.2
Methylmorpholine, $CH_3N(C_2H_4)_2O$	0.9051	115.4	16.0
Phenylmorpholine, $C_6H_5N(C_2H_4)_2O$	——	260.0	..
Morpholine ethanol, $HOC_2H_4N(C_2H_4)_2O$	1.0724	225.7	0.11
Morpholine ethyl ether, $C_2H_5OC_2H_4N(C_2H_4)_2O$	0.9648	206.2	--
Morpholine vinyl ether, $C_2H_3OC_2H_4N(C_2H_4)_2O$	1.0023	210.1	0.3

SOLVENT PROPERTIES OF MORPHOLINES

Morpholine is miscible in all proportions with water, alcohol, glycols, glycol ethers, acetone, methyl butyl ketone, ethyl ether, butyl ether, benzene, turpentine, pine oil, castor oil, linseed oil, paraffin wax (hot) and saturated brine. It dissolves over 5 per cent of naphtha, shellac, rosin, ester gum, copal gum, a number of vinyl resins, cellulose acetate or nitrate, benzyl cellulose, alcohol-soluble and oil-soluble dyes. It will dissolve from 1 to 5 per cent of sulphur but less than 1 per cent of paraffin oil, beeswax, or water-soluble dye.

Morpholine ethanol has the same solvent properties as morpholine with the following exceptions: it dissolves less than 1 per cent of naphtha, from 1 to 5 per cent of rosin, over 5 per cent of linseed oil and forms gels with several vinyl resins.

Morpholine ethyl ether is an even more general solvent than morpholine as it adds naphtha and paraffin oil to the "miscible in all proportions" list, given for the latter. It dissolves from 1 to 5 per cent of paraffin wax, beeswax and Vinylite A. Over 5 per cent of gum dammar may be dissolved, whereas the gum is only soluble in part in the other morpholines. Two other differences from the morpholine characteristics are to be noted, viz., less than 1 per cent of water-soluble dye or cellulose acetate are dissolved in this ether. It may serve as a corrosion inhibitor in water solutions, as a light stabilizer for trichloroethylene, as an antiknock agent for gasoline, as a carbon remover for use on aluminum pistons, and possibly as an assisting agent in permanent waving.

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[253] H. Ulrich and J. Nuesslein, U. S. P. 1,923,179, Aug. 22, 1933; *Chem. Abs.*, 1933, 27, 5207.

[254] A. L. Wilson, *Ind. Eng. Chem.*, 1935, 27, 867; *Brit. Chem. Abs.* B, 1935, 893; *Chem. Abs.*, 1935, 29, 6571.

Of the morpholine derivatives the ethyl and vinyl ethers are the only compounds known to surpass morpholine in solvent power. Both ethers yield constant-boiling mixtures with water, a somewhat rare phenomenon considering their high boiling points. These solutions boil at about 99°C. and contain approximately 12 per cent amine. The vinyl ether is hydrolyzed completely in acid solution to morpholine ethanol and acetaldehyde.

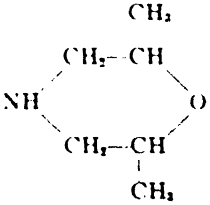
The ethyl ether is a mobile, colorless liquid and very stable. It has been suggested as a high-boiling reaction solvent in metatheses that set free acids and in the Grignard synthesis.

Phenylmorpholine, a white crystalline solid when pure, offers promise as a dye intermediate. It may serve as a coupling agent for diazotized compounds, especially in cases where the alkyl anilines are unstable due to migration of alkyl groups. Methyl morpholine, a non-reactive tertiary amine, has advantages as a solvent on account of its relatively low boiling point and density. It is less reactive than morpholine and more easily recovered. It may supply a substitute for ethyl ether or pyridine as a reaction solvent or as a catalyst.

A comparison of the vapor pressures for some morpholines with those of some aliphatic amines is given in Fig. 138.

DIMETHYLMORPHOLINE SYNTHESIS

Krasuskii[255] treated propene oxide with aqueous ammonia at 0-20°C. to obtain di-β-hydroxypropylamine, $(CH_3CHOHCH_2)_2NH$. This compound was then heated in a closed tube with 70 per cent sulphuric acid for 8 hours at 160-170°C. Steam distillation of the resultant reaction mixture, followed by caustic soda neutralization of the residue and steam distillation of the neutral liquor, yielded dimethylmorpholine.



The boiling point of the above compound (d_4^0 0.935), after purification by means of the hydrochloride salt and two distillations over metallic sodium, was 144°C. A yield of 4 g. of the morpholine was obtained by the above method from 16 g. of the dihydroxypropylamine.

Mono- and trihydroxypropylamines were prepared by Krasuskii in the course of the synthesis. The purified mono-amine (d_0^0 0.9769) boiled at 159.2-159.5°C. at 748 mm. The di-amine boiled at 249-250°C. (745 mm.) and had a melting point of 44.5-45.5°C. and d_{25}^{25} (liquid) 1.0038. The tri-amine (b.p. 190°C. at 23 mm.) melted at 48-50°C. and was soluble in water, ethyl alcohol and ether. Its hydrochloride melted at 186-188°C.

Attempts to prepare tetramethylmorpholine from isobutene oxide and hexamethylmorpholine from trimethylene oxide were unsuccessful.

[255] K. Krasuskii, *J. Gen. Chem. (U.S.S.R.)*, 1936, **6**, 460; *Brit. Chem. Abs.* **B**, 1936, 972; *Chem. Abs.*, 1936, **30**, 6377.

Propene Oxide and Derivatives

Propene oxide may be produced[256] by the direct oxidation of propene with oxygen in the presence of inert gases, e.g., nitrogen or carbon dioxide, at 300-375°C. under the catalytic influence of metals such as silver, silver and gold, or silver, gold and copper. Air may be used in the place of oxygen and a large proportion of carbon dioxide is recommended. The latter not only acts as a diluent but inhibits further reaction. The pressure used is above normal, in some cases as high as 50 atmospheres. The catalyst may be applied in the colloidal state in water. A typical reaction mixture was composed of 66 per cent oxygen and 24 per cent nitrogen. In one instance, colloidal silver (with small proportions of gold or copper or both) was placed in a high-pressure tube filled with water. After forcing propene gas into the water to form a solution, the tube was heated to 300-375°C., while air was pumped into the reaction vessel.

When propene oxide, and higher alkene oxides, are passed in vapor form over certain catalysts at elevated temperatures, isomerization to aldehydes takes place. Substances of large surface area, such as wood charcoal, active charcoal, alumina gel, silica gel and permutites, are suggested[257] for effecting this isomerization. Bauer[258] describes the conversion of propene oxide into propionaldehyde and other substances by passage in vapor form at 150-450°C. over catalysts. For this purpose he uses non-volatile, stable metallic compounds of oxygen-containing acids derived from elements of Groups 5 and 6, such as magnesium pyrophosphate associated with kieselguhr. According to Hoffmann,[259] propene oxide undergoes conversion into propionaldehyde to the extent of 70 per cent when passed in vapor form at 300°C. over silica gel or a silicate of large surface.

Alkene oxides of 3 to 4 carbon atoms, such as propene oxide and isobutene oxide, have been proposed as ingredients of an adhesive and softening composition for shoes.[260] Instead of isomerizing to propionaldehyde, propene oxide may be converted into allyl alcohol. It is reported by Young and Law[261] that passage of the diluted propene oxide vapor over a catalyst at 200-400°C. results in the production of this alcohol and propionaldehyde in approximately equal proportions. Nitrogen or steam may serve as the diluent and alumina, thoria or titania as the catalyst. Norton and Hass[261a] point out that propene oxide reacts with diethyl magnesium to furnish 2-pentanol, and with ethyl magnesium bromide to form a mixture of 2- and 3-pentanol.

n-Propyl Alcohol. On catalytic hydrogenation, propene oxide is converted exclusively into *n*-propyl alcohol. This somewhat unexpected reaction provides an excellent method for the synthesis of what is, from a practical viewpoint, a rather inaccessible alcohol. In the process of Young and Law,[262] the oxide diluted with steam is conducted over alumina at about 275°C. with a space velocity of 48-120 reciprocal hours. Subsequently, the gaseous mixture plus 4 volumes of hydrogen (calculated on the oxide fed) is led over a reduced-nickel catalyst at about 150°C.

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[256] French P. 785,149, 1935, to Soc. francaise de catalyse generalisee; *Chem. Abs.*, 1936, 30, 492. British P. 451,130, 1936; *Brit. Chem. Abs.* B, 1936, 971; *J. Inst. Pet. Tech.*, 1936, 22, 439A; *Chem. Abs.*, 1937, 31, 117.

[257] French P. 763,914, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 5468.

[258] K. Bauer, U. S. P. 2,031,200, Feb. 18, 1936, to Union Carbide & Carbon Corp.; *Chem. Abs.*, 1936, 30, 2200.

[259] U. Hoffmann, German P. 618,972, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, 30, 1066.

[260] British P. 408,245, 1934; *Chem. Abs.*, 1934, 28, 5612; addition to British P. 399,525; *Chem. Abs.*, 1934, 28, 1824. Both patents to United Shoe Machinery Corp.

[261] C. O. Young and G. H. Law, U. S. P. 1,917,179, July 4, 1933, to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* B, 1934, 393; *Chem. Abs.*, 1934, 28, 3744.

[261a] F. H. Norton and H. B. Hass, *J.A.C.S.*, 1936, 58, 2147; *Chem. Abs.*, 1937, 31, 364; *Brit. Chem. Abs.* A (2), 1937, 2.

[262] C. O. Young and G. H. Law, U. S. P. 1,953,548, Apr. 3, 1934, to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* B, 1935, 138; *Chem. Abs.*, 1934, 28, 3744.

Propene Dinitrate. By adding propene oxide very slowly to cooled fuming nitric acid and then pouring the mixture into hot water, Henry[263] obtained an oily, colorless liquid he termed propene dinitrin and gave $C_3H_6(NO_3)_2$ as its formula. A dinitrate was produced from amylene oxide by a similar procedure.

Amines. Combination of propene oxide with aqueous ammonia produces mono-, di- and triisopropanolamines as well as more complex substances formed by reaction of the hydroxyl groups of these bases. Wickert[264] explains that the production of the latter compounds may be minimized by maintaining the temperature at or below 55°C. It is also desirable to avoid an excess of unchanged oxide in the mixture. Another process for the manufacture of isopropanolamines has been disclosed by Wickert[265] in which propene oxide is bubbled through porous porcelain into 28 per cent aqueous ammonia kept below 55°C. (45-55°C.). Use of an excess of oxide leads to violent exothermic reaction and further condensation of the products. When the proportion of propene oxide is about 80 per cent of that required to form the tri-compound, the resulting mixture of bases is stated to contain more than 90 per cent of triisopropanolamine as well as mono- and di-derivatives which can be recovered by vacuum distillation.

The use of anhydrous mono- or dipropanolamine for the removal of carbon dioxide from industrial gases has been described by Smola.[266] Like triethanolamine, tripropanolamine forms addition products and alcoholates by reaction with metallic salts such as cobalt chloride. A number of such metallic compounds have been prepared by Tettamanzi.[267] Complex derivatives made by condensation of propene and butene oxides with β,γ-dihydroxypropyl-*m*-toluidine and similar bases have been reported by Lange.[268] For example, (γ-methoxy-β-hydroxypropyl)-aminobenzene treated with butene oxide at 170-180°C. produces the hydroxybutyl derivative which boils at 205-208°C. (10 mm.).

Reaction products of propene oxide with ammonia or with organic hydroxy-, carboxy-, amino- or hydroxyalkylamino-compounds may be condensed at 100 to 150°C. with urea, thiourea, guanidine or their derivatives.[269] A derivative of guanidine-propene oxide may be used in printing vat dyes. Dihydroxypropylglycolic ether plus methyl guanidine furnishes a sizing agent for viscose rayon. Isopropyl urea combined with trihydroxyethyl sorbite produces a cleaning and emulsifying agent.

Numerous water-soluble condensation products applicable as assistants in the textile and related industries may be prepared by use of alkene oxides in single or successive combinations with aliphatic organic hydroxylated substances.[270] The latter should have at least 5 carbon atoms or should be amines having one reactive —NH group. The products may be rendered more soluble in water by sulphonation. As instances of the above condensations, cetyl alcohol, *n*-$C_{16}H_{33}OH$, may be combined with propene oxide in the proportion of 1:6 moles. After an addition of

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[263] L. Henry, *Ber.*, 1871, 4, 602; *J.C.S.*, 1871, 24, 808

[264] J. N. Wickert, Canadian P. 346,165, 1934, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, **29**, 2175.

[265] J. N. Wickert, U. S. P. 1,988,225, Jan. 15, 1935, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, **29**, 1439; *Brit. Chem. Abs.* B, 1935, 1130.

[266] A. Smola, *Eis-u. Kälte Ind.*, Feb., 1934, 1; *Kälte Ind.*, April, 1934, 46; *Bull. Intern. Inst. Refrigeration*, 1934, 15, 289; *Chem. Abs.*, 1935, **29**, 2789; *Brit. Chem. Abs.* B, 1935, 21.

[267] A. Tettamanzi, *Atti accad. sci. Torino, Classe sci. fis., mat. nat.*, 1935, **70**, 81; *Chem. Abs.*, 1935, **29**, 6164; *Brit. Chem. Abs.* A, 1935, 849.

[268] H. Lange, German P. 610,799 and 610,798, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 5860. British P. 442,024, 1934; *Brit. Chem. Abs.* B, 1936, 310.

[269] British P. 443,436, 1935; *Brit. Chem. Abs.* B, 1936, 486. French P. 792,846, 1936; *Chem. Abs.*, 1936, **30**, 4240. Both patents to I. G. Farbenind. A.-G.

[270] British P. 443,559, 443,631 and 443,632, 1935, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1936, 684; *Chem. Abs.*, 1936, **30**, 5329.

2 moles of ethylene oxide, the product may be treated with chlorosulphonic acid in carbon tetrachloride at below 10°C. Similarly, stearic acid, treated in turn with 3 molar proportions each of ethylene, propene and then ethylene oxides, supplies a material for softening and finishing viscose rayon. If 1 part of cetylamine is reacted with 4 of ethylene oxide and again with 12 to 16 parts of propene oxide, the condensate may be utilized in dyeing wool.

The reactivity of such diverse materials as silk, wool, furs, feathers, fibroin silk, casein and gelatine toward acid-treating agents is said to be increased by the action of alkene oxides or their derivatives on them.[271]

Cellulose hydroxypropyl phthalate and similar hydroxy aliphatic esters of various dicarboxylic acid esters of cellulose have been produced by Malm and Fordyce.[272] Cellulose phthalate is allowed to react with propene oxide for 24 hours at 100°C. to secure the above mentioned ester. Hydroxyalkyl derivatives of cellulosic materials such as cotton or a bisulphite pulp in sheets may be obtained by interaction with an alkene oxide in the absence of bases, provided a catalytic salt is present.[273] Contact media suggested for the purpose are as follows: an alkali metal, zinc acetate or chloride, magnesium chlorate, calcium or barium sulphocyanide, or a halide of a heterocyclic tertiary amine, such as benzylpyridinium chloride. The cellulose derivatives may be formed into sheets or used for esterification.

THE HIGHER OLEFIN OXIDES

Few of the higher aliphatic olefin oxides have received close study, probably on account of the difficulty of their preparation. In this connection it is interesting to note that small amounts of olefin oxides (probably butene-2 oxide) have been found in the products of oxidation of butene-2 with oxygen in Pyrex tubes at 375-490°C.[274]

Batalin and Ugryumov[275] secured a 76-81 per cent yield of butene-2 oxide by interaction of the corresponding halohydrin with 40-50 per cent aqueous sodium hydroxide at 75-90°C. The product boiled at 55-58°C. and had d_0^0 0.8306. Brockway and Cross[275a] report that *cis*-butene-2 oxide boils at 54°C. at 747 mm. while *trans*-butene-2 oxide boils at 60°C. under the same pressure. Isomerization of the oxide in aqueous solution at 150°C. furnished methylethyl ketone. Treatment with 5 moles of ammonia (as a 25 per cent aqueous solution) gave, after 100 hours at 38°C., 41.5 per cent mono- and 40 per cent dibutanolamine. The proportion of the mono derivative could be increased to 66 per cent when 3 moles of the oxide and 1 mole of (aqueous) ammonia were interacted for 6 hours at 100°C. Both amines were soluble in water, ether and alcohol. Tributanolamine, a viscous colorless mass, was only slightly soluble in water, and its solubility decreased with increase in temperature. The boiling points and densities of the three butanolamines are given in Table 123.

On reacting with diethylmagnesium, butene-2 oxide was said to form 3-methyl-2-pentanol.[275b]

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[271] French P. 794,750, 1936, to Aceta G.m.b.H.; *Chem. Abs.*, 1936, **30**, 5334.

[272] C. J. Malm and C. R. Fordyce, U. S. P. 2,051,219, Aug. 18, 1936, to Eastman Kodak Co.; *Chem. Abs.*, 1936, **30**, 6942.

[273] P. Berger and A. F. Bidaud, U. S. P. 2,047,189, July 14, 1936, to Soc. des usines chimiques Rhone-Poulenc; *Chem. Abs.*, 1936, **30**, 6195.

[274] H. J. Lucas, A. N. Prater and R. F. Morris, *J.A.C.S.*, 1935, **57**, 723; *Brit. Chem. Abs.* A, 1935, 728; *Chem. Abs.*, 1935, **29**, 3649.

[275] V. S. Batalin and P. G. Ugryumov, *Sintet. Kauchuk*, 1936, No. 6, 8; *Chem. Abs.*, 1936, **30**, 6701.

[275a] L. O. Brockway and P. C. Cross *J.A.C.S.*, 1936, **58**, 2407; *Chem. Abs.*, 1937, **31**, 1002.

[275b] F. H. Norton and H. B. Hass, *J.A.C.S.*, 1936, **58**, 2147; *Chem. Abs.*, 1937, **31**, 364; *Brit. Chem. Abs.* A (2), 1937, 2. D. L. Cottle and L. S. Powell, *J.A.C.S.*, 1936, **58**, 2267, *Chem. Abs.*, 1937, **31**, 363; *Brit. Chem. Abs.* A (2), 1937, 3.

TABLE 123.—*Boiling Points and Densities of Butanolamines.*

	Boiling Point	d_{20}^{20}
Monobutanolamine	159-160°C. (at 745 mm.)	0.9416
Dibutanolamine	240-250°C. (at 753 mm.) 150-152°C. (at 20 mm.)	0.9809
Tributanolamine	200-201°C. (at 20 mm.)	0.9975

Walti[276] obtained the oxides of butene-1 and pentene-1 by the action of hot aqueous alkali on 1-chlorobutanol-2 and 1-chloropentanol-2, respectively. Hexene-1,2-oxide was prepared by refluxing the corresponding chlorohydrin in anhydrous ether solution with powdered potassium hydroxide. Walti found that pentene-1,2-oxide reacts readily with a 30 per cent aqueous solution of dimethylamine to yield 1-dimethylaminopentanol-2. Hexene-1,2-oxide combines rapidly with 48 per cent hydrobromic acid in the cold and is thus converted into 1-bromohexanol-2. The combination of isobutene oxide with dibenzylamine has been shown to furnish 1-dibenzylamino-2-methyl-2-propanol.[277]

Like the lower olefin oxides, some of the higher members undergo isomerization to the corresponding aldehydes or ketones. When heated with zinc chloride at 315°C., pentene-2,3-oxide and heptene-3,4-oxide are isomerized to methyl-*n*-propyl ketone and ethyl-*n*-butyl ketone, respectively.[278]

The products of the reaction between magnesium dimethyl or diethyl with cyclohexene oxide at 100°C. in ethereal solution consist, after hydrolysis, of *trans*-2-methylcyclohexanol or *trans*-2-ethylcyclohexanol, respectively.[279]

Cyclohexene oxide has been produced by Bartlett[280] on treatment of the *trans*-chlorohydrin of cyclohexene with cold methyl alcohol. When the oxide was treated with hydrogen chloride or cyclohexene with hypochlorous acid, the *trans* form of the cyclic chlorohydrin was obtained.

The oxide of $\Delta^{1,3}$-cyclohexadiene has been prepared from the dibromide of the cyclic compound by Bedos and Ruyer.[281] The dihalogen derivative was submitted to successive treatments with silver acetate and dry powdered potassium hydroxide in diethyl ether. The oxide was found to react slowly with perbenzoic acid to form the dioxide. It was not possible to decolorize bromine in carbon tetrachloride immediately with the oxide except in the presence of a little water. By treatment of the oxide with phosphorus pentabromide in ether, the original dibromide (m.p. 108°C.) could be regained as well as a liquid isomer.

The higher olefin oxides have, so far, attracted little attention either from scientific or industrial investigators. However, a few derivatives of these substances have been suggested for use in special applications.

The condensation of isobutene oxide with anhydrous alcohols, e.g., methyl or ethyl, can be effected by heating in the presence of a catalyst such as sulphuric, nitric or phosphoric acids. The products are the corresponding monoalkyl ethers of isobutene glycol, which boil above 140°C. and are said to be applicable as solvents for gums, resins, lacquers and cellulose esters.[282]

Dreyfus[283] proposes to make a material which can be used in the manufacture of rayon films and lacquers by reacting an alkene oxide, for instance, butene oxide, with a mixed aliphatic ester of cellulose.

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[276] A. Walti, *J.A.C.S.*, 1934, **56**, 2723; *Brit. Chem. Abs.* **A**, 1935, 193; *Chem. Abs.*, 1935, **29**, 731.

[277] Ya. O. Gabel, *Bull. soc. chim.*, 1934, (5) 1, 1006; *Chem. Abs.*, 1935, **29**, 750.

[278] M. Favorskii, M. Chichonkin and I. Ivanov, *Compt. rend.*, 1934, **199**, 1229; *Brit. Chem. Abs.* **A**, 1935, 194; *Chem. Abs.*, 1935, **29**, 1388.

[279] P. D. Bartlett and C. M. Berry, *J.A.C.S.*, 1934, **56**, 2683; *Brit. Chem. Abs.* **A**, 1935, 208; *Chem. Abs.*, 1935, **29**, 746.

[280] P. D. Bartlett, *J.A.C.S.*, 1935, **57**, 224; *Chem. Abs.*, 1935, **29**, 1785; *Brit. Chem. Abs.* **A**, 1935, 486.

[281] P. Bedos and A. Ruyer, *Compt. rend.*, 1936, **202**, 671; *Brit. Chem. Abs.* **A**, 1936, 598; *Chem. Abs.*, 1936, **30**, 3789.

[282] K. R. Edlund, U. S. P. 1,968,032, July 31, 1934, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 5832; *Brit. Chem. Abs.* **B**, 1935, 618.

[283] H. Dreyfus, U. S. P. 2,033,820, Mar. 10, 1936; *Chem. Abs.*, 1936, **30**, 3232.

Compounds of butene oxide with calcium chloride are said to be useful as pest-destroying agents.[284] Butanolamine is mentioned as a suitable material for the removal of weak gaseous acids from coke-oven gas.[285]

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[284] British P. 426,398, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 5551; *Brit. Chem. Abs.* **B**, 1935, 608.

[285] British P. 417,379, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1935, 55; *Chem. Abs.*, 1935, **29**, 1234.

Chapter 24

Miscellaneous Reactions of Olefins (I)

A number of addition reactions of the simple olefins with sulphuric acid, halogens and halogen acids have already been discussed.[1] In the following account some further reactions of these olefins, mostly of an additive character also, will be described. Among the compounds with which olefins condense are included aromatic hydrocarbons, paraffins, naphthenes, phenols, acids, acid halides, ammonia, and amines.

CONDENSATION OF ALKENES WITH AROMATIC HYDROCARBONS

Many investigations have shown that the Friedel-Crafts reaction for the alkylation of aromatic hydrocarbons may take place with the intermediate formation of an addition complex.[2] The direct alkylation of aromatics by alkenes in the presence of acid catalysts is a particular reaction of these hydrocarbons which has received considerable attention. A discussion of such perhaps is best systematized on the basis of the catalysts employed. The more important of these are sulphuric acid, phosphoric acid, phosphorus pentoxide, aluminum chloride and boron fluoride.[3]

Use of Sulphuric Acid. Alkylation in the presence of this acid was first investigated by Kraemer and Spilker[4] and Brochet,[5] who showed that the acid provided a convenient procedure for the preparation of some alkyl benzenes. Brochet believed that the method was general, although his results were obtained with hexene and benzene. Ipatieff, Corson and Pines,[6] however, have observed that this reaction is not applicable for the ethylation of benzene even under pressure. They investigated the effect of using sulphuric acid of both 96 and 80 per cent concentration as catalysts for propylation of benzene, and found that with the more concentrated acid interaction was largely alkylation, with only slight ester formation. On the other hand, when 80 per cent acid was employed, alkylation and formation of the alkyl sulphate occurred to about the same degree. With isobutene and benzene and acid of 96, 80 and 70 per cent concentration, the predominant reactions were alkylation, polymerization of the olefin to triisobutylene and formation of alkyl sulphate, respectively. The extent of alkylation was shown to depend more or less on the concentration of the olefin in the reacting liquid. The results obtained when 96 per cent sulphuric acid was used as a catalyst for the propylation of benzene are given in Table 124.

Some of the higher alkenes, namely, butene-1, pentene, octene, nonene and dodecene, were substituted for propene. The structures of the products were not

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[1] See Chapters 11, 13, 14, 16, and 20, this text. Also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[2] See Chapter 6. *Cf.* also Chapter 17 in which alkylation of aromatics with secondary and tertiary alcohols is discussed.

[3] See also the discussion in Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[4] G. Kraemer and A. Spilker, *Ber.*, 1890, **23**, 3169; *J.C.S.*, 1891, **60**, 206.

[5] A. Brochet, *Compt. rend.*, 1893, **117**, 115; *J.C.S.*, 1893, **64** (I), 635; *Chem Zentr.*, 1893, **2**, 429.

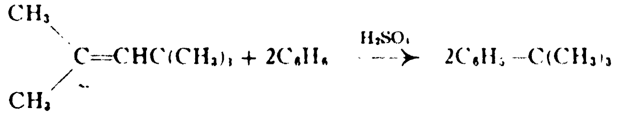
[6] V. N. Ipatieff, B. B. Corson and H. Pines, *J.A.C.S.*, 1936, **58**, 919; *Brit. Chem. Abs.* **A**, 1936, 975; *J. Inst. Pet. Tech.*, 1936, **22**, 395A; *Chem. Abs.*, 1936, **30**, 5191

TABLE 124.—*Propylation of Benzene.*

Run	Vol. of 96% H_2SO_4	Vol. of Benzene	Grams of Propene	Ratio of Mono- to Di-isopropylbenzene
1	100 cc.	200 cc.	110 g.	1.4
2	100 cc.	400 cc.	110 g.	3.9
3	250 cc.	1000 cc.	300 g.	6.3

determined in all cases. Diisopropyl-, di-*ter*-butyl- and di-*sec*-butyl-benzene, and isopropyltoluene, however, were all shown to have the substituents in the 1 and 4 positions by oxidation to either terephthalic or *p*-toluic acids or by nitration. Tetraisopropyl benzene (obtained in this investigation) was believed to be identical with the 1,2,4,5-derivative previously described by Berry and Reid.[7] The temperature at which alkylation was effected varied between 0 and about 20°C. in most cases. However, in the attempted propylation of benzene, using 80 per cent sulphuric acid as a catalyst, the reaction was allowed to proceed at 60°C. Furthermore, in preparing higher homologues from diisopropylbenzene, using 96 per cent acid, the temperature also was permitted to rise to 60°C. In treating naphtha fractions (boiling 90° to 95°C. and 125° to 130°C.) from brown coal with sulphuric acid of different concentrations, Geissler[8] employed a temperature of 10° to 15°C. The high boiling oils which were obtained when 90 per cent acid was used as a treating agent were found to be the condensation products of toluene with heptene and octene.

When alkylation of benzene was attempted using di- or tri-isobutylene with 96 per cent sulphuric acid as a catalyst, mono-, *p*-di- and higher *ter*-butyl-benzenes were obtained. Ipatieff and Pines referred to this type of reaction as a "depolyalkylation."



$$(CH_3)_2C{=}CHC(CH_3)_3 + 2C_6H_6 \xrightarrow{H_2SO_4} 2C_6H_5{-}C(CH_3)_3$$

As an example, 140 g. of diisobutylene and 97 g. of benzene were added during about 1½ hours to 100 cc. of 96 per cent sulphuric acid in a flask cooled by an ice bath. The reaction mixture separated into two layers. The hydrocarbon layer weighed 214 g. after washing and drying. Fractions corresponding to mono-, di- and tri-*ter*-butyl benzene were obtained by distillation. Similar results were also secured using aluminum chloride as the catalyst.[9]

Truffault[10] has reported the alkylation of benzene by cyclohexene in the presence of concentrated sulphuric acid. The reaction proceeds according to the following equation:

$$C_6H_6 + C_6H_{10} \xrightarrow{H_2SO_4} \underset{(b.p.,\ 104\text{-}106°C.)}{C_6H_5{-}C_6H_{11}} + \xrightarrow{C_6H_{10}} \underset{\substack{p\text{-dicyclohexylbenzene} \\ (m.p.,\ 102\text{-}103°C.)}}{C_6H_{11}{-}C_6H_4{-}C_6H_{11}}$$

He also found that it was possible to cause a condensation of halogenated ethylene derivatives with benzene to form ω-haloalkylbenzenes of interest in synthetic work, particularly in the preparation of amides and carboxylic acids.

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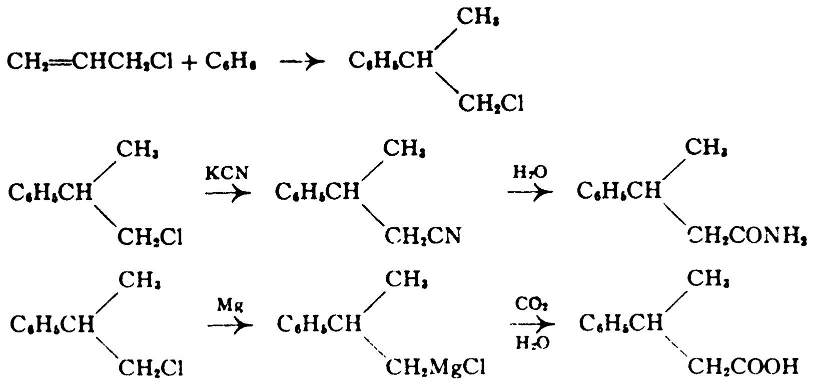
[7] T. M. Berry and E. E. Reid, *J.A.C.S.*, 1927, **49**, 3142; *Chem. Abs.*, 1928, **22**, 394; *Brit. Chem. Abs.* **A**, 1928, 161.

[8] M. Geissler, *Braunkohlenarch.*, 1935, No. *43*, 1; *Chem. Abs.*, 1936, **30**, 3992.

[9] V. N. Ipatieff and H. Pines, *J.A.C.S.*, 1936, **58**, 1056; *J. Inst. Pet. Tech.*, 1936, **22**, 395A; *Chem. Abs.*, 1936, **30**, 5190; *Brit. Chem. Abs.* **A**, 1936, 976. *Cf.* Chapter 6.

[10] R. Truffault, *Compt. rend.*, 1936, **202**, 1286; *Brit. Chem. Abs.* **A**, 1936, 832; *Chem. Abs.*, 1936, **30**, 4154.



$$CH_2{=}CHCH_2Cl + C_6H_6 \longrightarrow C_6H_5CH\begin{array}{l}CH_3\\CH_2Cl\end{array}$$

$$C_6H_5CH\begin{array}{l}CH_3\\CH_2Cl\end{array} \xrightarrow{KCN} C_6H_5CH\begin{array}{l}CH_3\\CH_2CN\end{array} \xrightarrow{H_2O} C_6H_5CH\begin{array}{l}CH_3\\CH_2CONH_2\end{array}$$

$$C_6H_5CH\begin{array}{l}CH_3\\CH_2Cl\end{array} \xrightarrow{Mg} C_6H_5CH\begin{array}{l}CH_3\\CH_2MgCl\end{array} \xrightarrow[H_2O]{CO_2} C_6H_5CH\begin{array}{l}CH_3\\CH_2COOH\end{array}$$

Naphthalene is said to be propylated by reaction with propene in the presence of naphthalene sulphonic acid[11] or of sulphuric acid. Naphthalene sulphonic acid itself may also be propylated in this way.[12] The products obtained by the condensation of cycloolefins (b.p. from 85° to 120°C.) and naphthalene are said to be useful for breaking petroleum emulsions.[13] On the other hand, Schildwächter[14] has stated that a good lubricating oil may be prepared by the condensation of ethylene with a coal-tar fraction boiling between 200° and 300°C. The viscosity was still further increased by treatment with the silent electric discharge. Oil made by this method was reported to show stability against oxidation and high temperatures.

Ipatieff[15] has described several procedures for increasing antiknock properties of gasoline by treating straight-run or cracked distillates with the gases from cracking operations and catalysts of either sulphuric acid or acid sludges. Some alkylated compounds are said to be formed. He has also suggested[16] that the reaction of aromatic hydrocarbons with olefins in the presence of sulphuric acid may be used to remove gum-forming olefins from fuel gases. After the treatment both the purified gas and the aromatic derivatives are utilized. Ipatieff[17] has recommended a mixture of sulphuric and phosphoric acids to catalyze the alkylation of a cyclic hydrocarbon (such as benzene) by olefinic substances, e.g., propene or cracking gas. The products could be employed in motor fuels. He has also used phosphoric acid to remove sulphuric acid esters dissolved in the hydrocarbon liquid after alkylation of an aryl hydrocarbon with a sulphuric acid catalyst.[18]

Use of Phosphoric Acid. Alkylated aromatics which had good antiknock properties were obtained by treating benzene with the gases from oil-cracking, using phosphoric acid as the contact agent.[19] The influence of the latter compound on condensations involving low-molecular weight olefins has been studied by Ipatieff, Pines and Komarewsky.[20] They reported that ethylation could be effected using this catalyst at 300°C. For example, a reaction was carried out in a glass-lined, electrically-heated, rotating autoclave. For a run employing 314 g. of benzene in a container of 3 liters capacity, ethylene was added until the total pressure was 60 atmospheres at 21°C. The catalyst was 103 g. of 85 per cent phosphoric acid. Reaction continued for 12 hours, and 569 g. of liquid product were obtained. This was fractionated and gave mono-, di-, tri- and tetra-ethyl benzenes. The structures of the di- and tri-derivatives were shown to correspond to the 1,3- and 1,3,5-compounds, respectively.

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[11] R. M. Isham, U. S. P. 2,014,766, Sept. 17, 1935, 75 per cent to W. B. Pine; *Chem. Abs.*, 1935, **29**, 7346; *Brit. Chem. Abs.* **B**, 1936, 921; *J. Inst. Pet. Tech.*, 1936, **22**, 53A.

[12] R. M. Isham, U. S. P. 2,017,803, Oct. 15, 1935, 75 per cent to W. B. Pine; *Chem. Abs.*, 1935, **29**, 8000; *Brit. Chem. Abs.* **B**, 1936, 1142.

[13] M. de Groote, U. S. P. 1,985,720, Dec. 25, 1934, to Tretolite Co.; *Brit. Chem Abs.* **B**, 1935, 1127; *Chem. Abs.*, 1935, **29**, 1238.

[14] H. Schildwächter, *Angew. Chem.*, 1934, **47**, 677; *Chem. Abs.*, 1935, **29**, 328; *J. Inst. Pet Tech.*, 1934, **20**, 576A.

[15] V. Ipatieff, U. S. P. 2,001,906, 2,001,907, 2,001,908, 2,001,909, and 2,001,910, May 21, 1935, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1935, 486, 681, 917; *J. Inst. Pet. Tech.*, 1935, **21**, 267A; *Chem. Abs.*, 1935, **29**, 4573.

[16] V. Ipatieff, U. S. P. 2,035,889, March 31, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 3624; *J. Inst. Pet. Tech.*, 1936, **22**, 296A.

[17] V. Ipatieff, U. S. P. 2,006,695, July 2, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 5456; *Brit. Chem. Abs.* **B**, 1936, 630.

[18] V. Ipatieff, U. S. P. 2,039,798, May 5, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 4175.

[19] V. Ipatieff, U. S. P. 2,005,861, June 25, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 5647. For the treatment of gasolines (having a high content of aromatics) with olefin-containing gases in the presence of pyrophosphoric acid, see V. Ipatieff, U. S. P. 2,067,764, Jan. 12, 1937, to Universal Oil Products Co.; *Chem. Abs.*, 1937, **31**, 1603.

The alkylation of higher homologues was also carried out successfully. Ethylation of naphthalene and tetrahydronaphthalene was accomplished under pressure at 300°C. using 85 per cent phosphoric acid. Propylation was effected with 89 per cent acid and a temperature of 200°C. Almost 90 per cent of the propene was taken up by naphthalene, although 27 g. of fluorene gave only 9 g. of propyl fluorene when treated with 40 g. of propene and 25 g. of acid.

Phosphorus Pentoxide as Catalyst. Previous to the work of Ipatieff, Pines and Komarewsky on phosphoric acid, Malishev[21] had observed the catalytic effect of phosphorus pentoxide on the alkylation of benzene. For example, 708 g. benzene, 50 g. phosphorus pentoxide, 24 g. lampblack (to maintain the catalyst in colloidal suspension) and 10 g. cresol (to peptize the lampblack) were heated for 100 minutes at 250°C. with agitation, and ethylene added in sufficient quantity to maintain a pressure of 27 atmospheres. The product, 527.7 g. of liquid, was fractionally distilled. The volume per cent composition of the distillate was: 1.6 per cent benzene, 18.2 per cent ethyl benzene, 42.3 per cent diethyl benzene, 24.4 per cent triethyl benzene and 8.5 per cent of higher isomers. From the last fraction, 34 g. of hexaethyl benzene was isolated. Experiments were also conducted employing benzene and isobutene, toluene and propene, and naphthalene and ethylene. Reaction in each instance was carried out in essentially the manner just described. The temperature was kept between 200 and 250°C., except in the propylation of toluene which was carried out at 150°C. to give *p*-cymene. The only product from these experiments which was identified was 1,4-*di-ter*-butyl benzene (m.p. 76°C.).

Treatment of cracked gasoline with phosphorus pentoxide (and carbon black) may be employed as a method of refining.[22] This procedure appears to comprise alkylation of the aromatic and naphthenic constituents as well as polymerization of the olefins. There is an increase in octane rating and decrease in bromine number of a distillate refined in this manner, as is shown in Table 125.

That there is a difference between the effects of phosphorus pentoxide and metaphosphoric acid is shown by the polymerization of ethylene by the former under 50 atmospheres pressure and at 250°C. to a gasoline-like liquid containing many types of hydrocarbons. This polymerization, however, apparently is hindered when aromatic hydrocarbons are present and may even be reversed, since under these conditions diisobutylene gives rise to, for example, isobutyl benzene. Refining may be carried out by distilling the gasoline through a stirred suspension of 1 to 2 per cent phosphorus pentoxide in a heavy unrefined mineral oil.

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[20] V. N. Ipatieff, H. Pines and V. I. Komarewsky, *Ind. Eng. Chem.*, 1936, **28**, 222; *Brit. Chem. Abs.* **B**, 1936, 309; *J. Inst. Pet. Tech.*, 1936, **22**, 142A.

[21] B. W. Malishev, *J.A.C.S.*, 1935, 57, 883; *Chem. Abs.*, 1935, **29**, 4335; *J. Inst. Pet. Tech.*, 1935, **21**, 254A; *Brit. Chem. Abs.* **A**, 1935, 852. *Cf.* B. W. Malishev, British P. 437,072, 1935, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1936, 91; *J. Inst. Pet. Tech.*, 1936, **22**, 23A; *Chem. Abs.*, 1936, **30**, 2204. French P. 782,194, 1935; *Chem. Abs.*, 1935, **29**, 6905.

[22] B. W. Malishev, *Ind. Eng. Chem.*, 1936, **28**, 190; *J. Inst. Pet. Tech.*, 1936, **22**, 155A. Canadian P. 357,206, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 4001. See also, Canadian P. 355,081, 1935; *Chem. Abs.*, 1936, **30**, 1991. French P. 793,250, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 4514.

TABLE 125.—*Treatment of Gasoline with Phosphorus Pentoxide.*

	Untreated Distillate	Distillate Treated With 0.1% P_2O_5
Initial b.p., °C.	39	40
Final b.p., °C.	234	225
Color Saybolt	Yellow	30 +
Air-jet gum (glass), mg./100 cc.	—	0.2
Induction period (accelerated oxidation test)	30 min.	4 hr. +
Air-jet gum after induction, mg./100 cc.	—	4.4
Octane number (motor method)	67.0	73.0
Bromine number	81	54.0

The effect of phosphoric anhydride on unsaturated compounds has also been observed by Truffault.[23] He found that extraction of the oxide with cyclohexene (in a Soxhlet apparatus) gave 80 to 90 per cent of cyclohexylcyclohexene [b.p. (760 mm.) 238-239°C., n_D^{20} 1.493, d^{20} 0.904]. With ethylene or propene and benzene it was possible to obtain the corresponding alkylated benzenes, but substitution of these olefins by pentene or cyclohexene gave mostly dimers of the latter.[24]

Application of Aluminum Chloride. In addition to its well-known use as a catalyst in the Friedel-Crafts reaction, aluminum chloride may be employed in the alkylation of aromatics by olefins, particularly for the preparation of monoalkyl[25] and monocyclohexyl benzenes.[26] Deposited on a siliceous carrier, the metallic chloride has served as a contact agent for the formation of alkyl benzenes in gasolines to improve the antiknock qualities of the latter.[27] When mixed olefins are the alkylating agents it is suggested that interaction between aromatics and the higher unsaturated hydrocarbons be carried out in the presence of sulphuric acid, after which any residual ethylene can then be combined with the cyclic compounds by the aid of aluminum chloride.[28]

Another method which has been proposed comprises partially chlorinating a paraffin, eliminating hydrogen chloride from the chloro compound by heating with ferric chloride and condensing the resulting olefin with an aromatic compound.[29] Nitrogen-containing cyclic substances, e.g., carbazole, are said to be alkylated at 50° to 200°C .in the presence of aluminum or ferric chloride to mono- or polyalkyl derivatives of an oily or resinous character.[30]

Materials for addition to lubricating oils have been prepared by treating polynuclear aromatics with olefins (using 20 per cent or more of aluminum chloride) at 50° to 250°C. The product is then hydrogenated to give a mixture of compounds which is reported to induce fluorescence when dissolved in hydrocarbon oils.[31] According to Shaffer and Fasce,[32] anthracene is added to the extract from the treatment of petroleum distillates with liquid sulphur dioxide and the mixture heated with aluminum chloride at 100° to 200°F. for several hours. Hydrolysis is then effected at 180°F. by agitation with aqueous hydrochloric acid. The slurry is filtered and the filtrate washed with water. The product is then dried and distilled to yield a material which is said to give a green fluorescence to lubricating oils and to improve the cast and pour point as well.

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[23] R. Truffault, *Compt. rend.*, 1935, **200**, 406; *Chem. Abs.*, 1935, **29**, 2927; *Brit. Chem. Abs.* **A**, 1935, 480.

[24] R. Truffault, *Compt. rend.*, 1936, **202**, 1286; *Chem. Abs.*, 1936, **30**, 4154; *Brit. Chem. Abs.* **A**, 1936, 832.

[25] J. G. Davidson, U. S. P. 1,953,702, Apr. 3, 1934, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1934, **28**, 3742; *Brit. Chem. Abs.* **B**, 1935, 140.

[26] L. F. Martin and G. H. Coleman, U. S. P. 1,969,984, to Dow Chemical Co.; *Chem. Abs.*, 1934, **28**, 6156; *Brit. Chem. Abs.* **B**, 1935, 716.

[27] G. Egloff, U. S. P. 2,009,108, July 23, 1935, to Universal Oil Products Co.; *Brit. Chem Abs.* **B**, 1936, 728; *Chem. Abs.*, 1935, **29**, 6041. See also, U. S. P. 2,010,948 and 2,010,949, Aug. 13, 1935; *Chem. Abs.*, 1935, **29**, 6606; *J. Inst. Pet. Tech.*, 1935, **21**, 382A.

[28] V. Ipatieff and A. V. Grosse, U. S. P. 1,994,249, Mar. 12, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 2974; *Brit. Chem. Abs.* **B**, 1936, 921; *J. Inst. Pet. Tech.*, 1936, **22**, 53A.

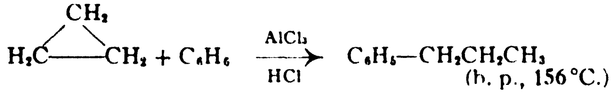
[29] C. A. Thomas, U. S. P. 1,995,827, March 26, 1935, to Sharples Solvent Corp., *Brit. Chem. Abs.* **B**, 1936, 443; *Chem. Abs.*, 1935, **29**, 3349.

[30] R. Michel, U. S. P. 1,972,232, Sept. 4, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 6444.

[31] British P. 409,696, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1934, 664; *J. Inst. Pet. Tech.*, 1934, **20**, 427A; *Chem. Abs.*, 1934, **28**, 6295. French P. 762,002, 1934; *Chem. Abs.*, 1934, **28**, 4590. See also, H. Hartmann and H. Rabe, U. S. P. 2,071,521, Feb. 23, 1937, to I. G. Farbenind. A.-G.

[32] S. A. Shaffer and E. V. Fasce, U. S. P. 1,988,753, Jan. 22, 1935, to Standard Oil Development Co.; *J. Inst. Pet. Tech.*, 1935, **21**, 139A; *Chem. Abs.*, 1935, **29**, 1622. Canadian P. 341,708, 1934; *Chem. Abs.*, 1934, **28**, 5225.

Cyclopropane is very similar in its reactions to an unsaturated hydrocarbon, and Grosse and Ipatieff[33] have found that it undergoes the same type of reaction with aromatics as do olefins, namely, the formation of an alkylated derivative. The product, however, instead of being a branched-chain substance is the *n*-alkyl derivative formed in the following manner:



Interaction may proceed to complete alkylation, and the hexapropylbenzene (m.p., 103°C.; b.p., 325°C.) has actually been isolated.

Although aluminum chloride is probably the most generally used metallic chloride, nevertheless Grosse and Ipatieff[33a] call attention to the application of other catalysts of this type. These include beryllium chloride, the tetrachlorides of titanium, zirconium and hafnium, and the pentachlorides of columbium and tantalum. Of these the titanium salt was the least effective.

Boron Trifluoride as Catalyst. This compound has been used as a catalyst for polymerization and other reactions of olefins[34] and in general is similar to aluminum chloride in its effect. For example, it is said to be possible to obtain intermediates for dyes or for the manufacture of wetting agents by treating an olefin and an aromatic hydrocarbon with the substances obtained by interaction of boron trifluoride with water, an alcohol or an acid.[35] Slanina, Sowa and Nieuwland[36] have reported that boron trifluoride accelerated the alkylation of benzene by propene. The greatest extent of reaction was obtained using either phenol or sulphuric acid with the halide. Other secondary catalysts (or promoters) were not so effective, but became increasingly so as their acidity increased. Thus, trichloroacetic acid was somewhat more active when used with boron trifluoride than was acetic acid. The important difference which was observed between the boron and aluminum halides was, whereas the latter gives a *m*-dialkyl compound, the former gives a *p*-dialkyl derivative.

Using sulphuric acid and boron trifluoride, Nieuwland and his co-workers succeeded in preparing isopropyl- and isobutylbenzenes, *p*-cymene (from toluene), and an isopropylnaphthalene of undetermined structure (b.p., 260-270°C.). It was found that ethylene did not work very well in these reactions. Ipatieff, Corson and Pines[37] found that sulphuric acid catalyzes the alkylation in the same manner as it does when admixed with boron trifluoride. However, Ipatieff and Grosse[38] reported later that boron trifluoride alone was also efficacious. For example, 250 cc. of benzene, 18.5 g. of the trifluoride and 2 g. of water were treated with ethylene at 20 atmospheres pressure for 8 hours at 20° to 25C°. More than 25 per cent of the aromatic was converted into monoethylbenzene (mainly), diethylbenzene and higher alkylated bodies. The effect of the acid-halide catalyst was studied further by Wunderly, Sowa and Nieuwland.[39] Experiments were conducted in the apparatus shown in Fig. 139, using 2 moles of benzene and adding propene at a carefully controlled rate. The temperature was 4°C.(±1°) and the time of contact 2 or 4 hours. In all instances, 80 g. of sulphuric acid were used (as catalyst) and in some cases 10 g. of boron trifluoride were added. The results are given in Table 126.

---

[33] A. V. Grosse and V. N. Ipatieff, Paper presented at American Chemical Society Meeting, Organic Division, Pittsburgh, Sept., 1936.

[33a] A. V. Grosse and V. N. Ipatieff, *J. Org. Chem.*, 1937, 1, 559.

[34] See Chapters 26 and 28. Also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

[35] French P. 799.016, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 7730. British P. 453.422, 1935; *Brit. Chem. Abs.* B, 1936, 1142; *J. Inst. Pet. Tech.*, 1936, **22**, 516A; *Chem. Abs.*, 1937, **31**, 1040.

[36] S. J. Slanina, F. I. Sowa and J. A. Nieuwland, *J.A.C.S.*, 1935, **57**, 1547; *Brit. Chem. Abs.* A, 1935, 1358; *Chem. Abs.*, 1935, **29**, 7296; *J. Inst. Pet. Tech.*, 1935, **21**, 407A.

[37] V. N. Ipatieff, B. B. Corson and H. Pines, *J.A.C.S.*, 1936, **58**, 919; *Brit. Chem. Abs.* A, 1936, 975; *Chem. Abs.*, 1936, **30**, 5191.

[38] V. N. Ipatieff and A. V. Grosse, *J.A.C.S.*, 1936, **58**, 2339; *Chem. Abs.*, 1937, **31**, 379; *J. Inst. Pet. Tech.*, 1937, **23**, 22A.

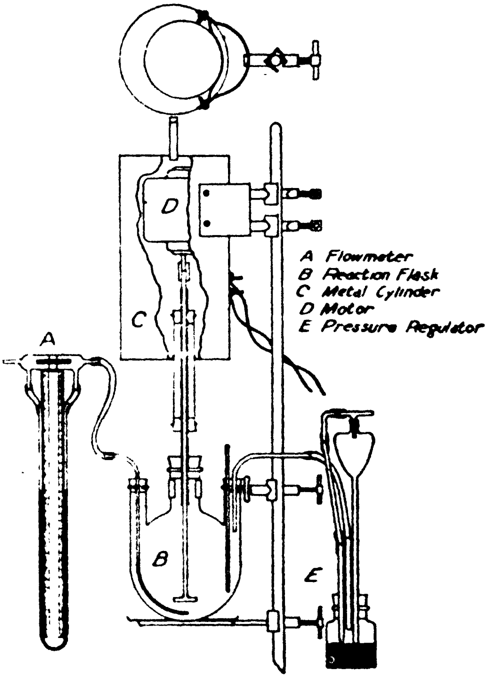


FIG. 139.
Apparatus Employed for Olefin-Benzene Condensations. (H. L. Wunderly, F. J. Sowa and J. A. Nieuwland)

Courtesy Journal of American Chemical Society

TABLE 126.—*Effect of Boron Trifluoride on Olefin-Benzene Reaction.*

Grams of H_2SO_4	Grams of BF_3	Time in Hours	Isopropylbenzene Obtained in Grams Mono-	Di-	Tri-
80.0	0.0	2	62.9	22.8	7.7
80.0	10.0	2	91.1	32.7	5.2
80.0	0.0	4	97.1	56.2	20.3
80.0	10.0	4	97.1	82.4	22.9

To determine the course of the reaction, benzene was refluxed with purified diisopropyl sulphate. At the end of an hour no layer had separated, and this was considered evidence that no interaction had occurred. Addition of a small proportion of sulphuric acid, however, caused violent combination to take place and the separation of a large layer. Brochet[40] suggested the mechanism (using α-hexene) to be represented by:

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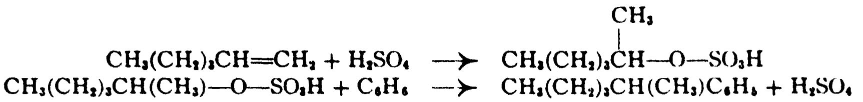
[39] H. L. Wunderly, F. J. Sowa and J. A. Nieuwland, *J.A.C.S.*, 1936, **58**, 1007; *J. Inst. Pet. Tech.*, 1936, **22**, 394A; *Brit. Chem. Abs.* **A**, 1936, 975; *Chem. Abs.*, 1936, **30**, 5191.



$$CH_3(CH_2)_3CH{=}CH_2 + H_2SO_4 \longrightarrow CH_3(CH_2)_3\overset{\overset{CH_3}{|}}{C}H{-}O{-}SO_3H$$
$$CH_3(CH_2)_3CH(CH_3){-}O{-}SO_3H + C_6H_6 \longrightarrow CH_3(CH_2)_3CH(CH_3)C_6H_5 + H_2SO_4$$

Wunderly, Sowa and Nieuwland disagreed with the last step. They believed that if this were the case, it should be possible to prepare *n*-propyl benzene if benzene were treated with *n*-propyl acid sulphate and di-*n*-propyl sulphate, using boron trifluoride as a catalyst. The products obtained in this way were not, however, *n*-propyl, but isopropyl benzenes and the proposed mechanism was therefore given as:

$$CH_3CH_2CH_2O{-}SO_3H \longrightarrow (C_3H_6) + H_2SO_4$$
$$(C_3H_6) + C_6H_6 \xrightarrow{(H_2SO_4)} (CH_3)_2CH{-}C_6H_5$$

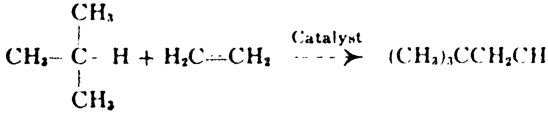
where (C_3H_6) represents an intermediate activated olefin stage which reacts readily with benzene.

CONDENSATION OF OLEFINS WITH PARAFFINS

Thermal decomposition of paraffins in the presence of catalysts to give a lower paraffin and an olefin has received considerable attention (see Chapters 2, 3, 4), but it has generally been considered that the reverse reaction would not occur very readily. Ipatieff and Grosse[41] have reported that paraffins, naphthenes, aromatics and olefins interact with surprising ease amongst themselves in the presence of halides of aluminum, boron, beryllium, titanium, zirconium, hafnium, thorium, columbium and tantalum. That change between paraffins and olefins takes place according to the general equation:

$$C_mH_{2m+2} + C_nH_{2n} \xrightarrow{\text{Catalyst}} C_{m+n}H_{2(m+n)+2}$$

or, as a specific example:



$$CH_3{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}H + H_2C{=}CH_2 \xrightarrow{\text{Catalyst}} (CH_3)_3CCH_2CH_3$$

However, combination proceeds as readily and smoothly as these equations suggest in only very few cases under very carefully controlled conditions. In most instances, complicating side-reactions occur. For example, the paraffin (C_nH_{2n+2}) formed initially may react with another molecule of ethylene to give a paraffin $(C_{n+2}H_{2n+6})$ which may continue to give higher homologues. In certain cases the paraffin may be split by the action of the catalyst to yield an olefin and another paraffin molecule. The former could then unite with a paraffin molecule to furnish a new aliphatic hydrocarbon.[42] This latter reaction is effected rather readily by aluminum chloride. Boron fluoride, on the other hand, was found to be a catalyst for the alkylation reaction, although it had no effect on paraffins and did cause polymerization of olefins. It was necessary, though, to have present some finely divided metal, such as nickel, and either water or anhydrous hydrogen fluoride.

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[40] A. Brochet, *Compt. rend.*, 1893, 117, 115; *Chem. Zentr.*, 1893, 2, 429; *J.C.S.*, 1893, 64 (1), 635.

[41] V. N. Ipatieff and A. V. Grosse, *J.A.C.S.*, 1935, 57, 1616; *Chem. Abs.*, 1935, 29, 7270; *Brit. Chem. Abs.* A, 1935, 1348; *J. Inst. Pet. Tech.*, 1935, 21, 406A. See also, V. Ipatieff and A. V. Grosse, U. S. P. 2,057,432, Oct. 13, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, 30, 8598.

[42] This reaction is called "auto-destructive alkylation." See Chapter 6.

Interactions of ethylene with isobutane, isopentane and 2,2,4-trimethylpentane and of isobutene and isobutane were effected in a high-pressure rotating autoclave of 800 cc. capacity (Fig. 140). The product in each run appeared to consist essentially of the expected paraffins of 2, 4, 6 or 8 more carbon atoms. Analysis was carried out by means of a Podbielniak column.[43] The gaseous reactants were weighed in small duraluminum autoclaves. Ethylene was introduced under a pressure of 20 kg. per sq. cm., and as this decreased because of the unsaturated hydrocarbon entering into combination with the other reactants, more was added. The results obtained in the experiments in which ethylene and isobutane were used are given in Table 127.

TABLE 127.—*Condensation of Ethylene and Isobutane.*

Experiment[a]	1	2	3	4	5	6
Isobutane charged (g.)	160	90	90	90	90	220
Isobutane reacted (g.)	24	88	88	89	88	180
Ethylene charged (g.)	81	130	115	110	90	104
Ethylene reacted (g.)	61	130	115	109	85	104
Boron fluoride used (g.)	2	8	8	14	14	30
Nickel used (g.)	5.0	5.0	5.0	10.0	10.0	5.0
Water used (g.)	0.50	2.0	2.0	4.0	4.0	25 g. HF
Time of reaction (hours)	32	28	26	21	22	40
Temperature (°C.)	20-25	20-30	20-30	20-25	20-25	20-25
Ratio of reacted C_2H_4 to reacted C_4H_{10} molecules	5.9:1	3.1:1	2.7:1	2.5:1	2.0:1	1.2:1
Refractive index of total product	1.4188	1.4126	1.4064	1.3998	1.3984	1.3819
437°F. end point gasoline in product %	37	60	82	85	90	97

[a] In Experiments 1-5 Pyrex glass liners, and in Experiment 6 a nickel liner, were used.

It is apparent from these data (Exp. 4, 5 and 1) that an increase in the ratio of boron trifluoride to the available paraffin increases the rate of alkylation. The product depends upon the relative number of molecules of ethylene absorbed per molecule of butane. There is also formed a semi-solid mass composed of catalysts together with an organic complex which is apparently the real accelerator. It reacts readily with water to give a layer of unsaturated hydrocarbons and a solution containing nickel salts of hydroborofluoric acid.

The liquid product was water-white and after washing and drying was shown to contain neither aromatics nor olefins. This indicated that reaction had taken place between the paraffin and olefin.

Ipatieff, Komarewsky and Grosse[44] have pointed out that boron trifluoride also has a somewhat different reactivity from aluminum chloride in bringing about combination of cycloalkanes with olefins. As with alkanes, condensation is only effected at a tertiary carbon atom, and hence boron trifluoride causes interaction of ethylene with either methylcyclopentane or methylcyclohexane, but not with cyclopentane or cyclohexane. Union takes place at 20° to 30°C. and at ethylene pressures between 5 and 15 atmospheres. There appears to be some polymerization of the olefin and splitting of the ring simultaneously with the alkylation.

When aluminum and hydrogen chlorides were used as a catalyst, alkylation was effected fairly readily according to the general reaction:

$$C_mH_{2m} + C_nH_{2n} \xrightarrow{\text{catalyst}} (C_mH_{2m-1})(C_nH_{2n+1})$$

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[43] See W. J. Podbielniak, *Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 119.

[44] V. N. Ipatieff, V. I. Komarewsky and A. V. Grosse, *J.A.C.S.*, 1935 57, 1722; *Chem. Abs.*, 1935, **29**, 7270; *Brit. Chem. Abs.* **A**, 1935, 1357; *J. Inst. Pet. Tech.*, 1935, 21, 407A. V. N. Ipatieff and A. V. Grosse (with V. I. Komarewsky), *J. Gen. Chem.* (*U.S.S.R.*), 1936, 6, 433; *Brit. Chem. Abs.* **A**, 1936, 975.

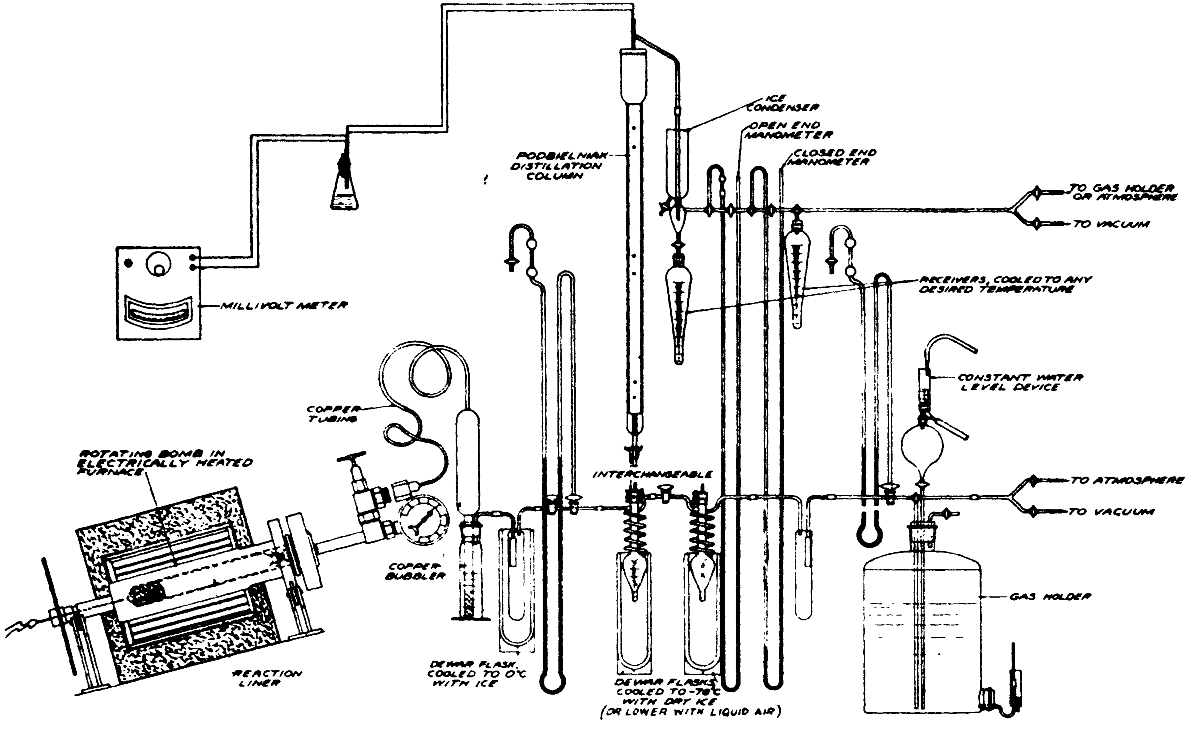
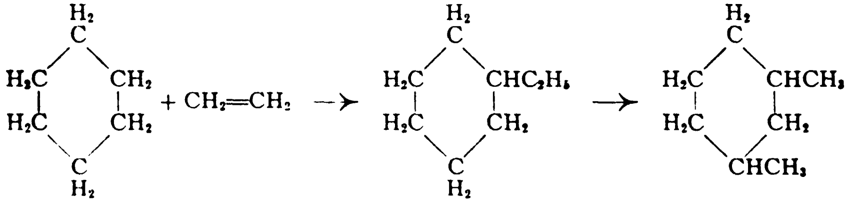

ICE CONDENSER
OPEN END MANOMETER
CLOSED END MANOMETER
PODBIELNIAK DISTILLATION COLUMN
TO GAS HOLDER OR ATMOSPHERE
TO VACUUM
MILLIVOLT METER
RECEIVERS, COOLED TO ANY DESIRED TEMPERATURE
CONSTANT WATER LEVEL DEVICE
COPPER TUBING
ROTATING BOMB IN ELECTRICALLY HEATED FURNACE
INTERCHANGEABLE
TO ATMOSPHERE
TO VACUUM
COPPER BUBBLER
GAS HOLDER
REACTION LINER
DEWAR FLASK COOLED TO 0°C WITH ICE
DEWAR FLASKS COOLED TO -78°C WITH DRY ICE (OR LOWER WITH LIQUID AIR)

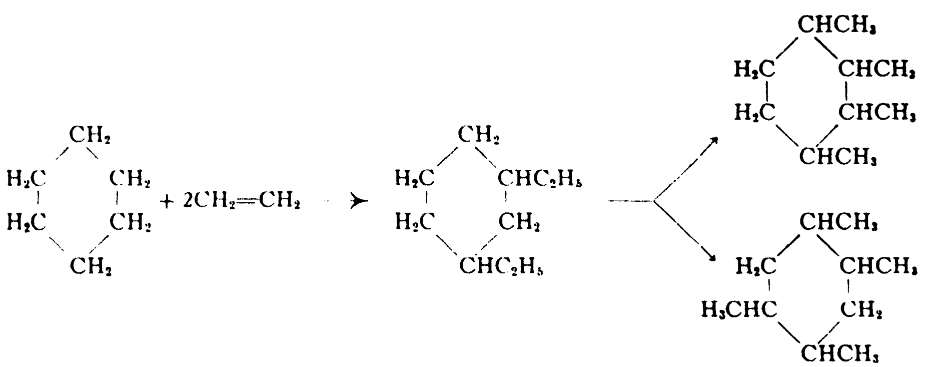
FIG. 140.—Apparatus Employed for Condensation of Olefins with Paraffins. (V. N. Ipatieff and A. V. Grosse)
Courtesy Journal of American Chemical Society

Frey and Hepp[45] report that the product secured from ethylene and propane, at 4500 lb. pressure and about 510°C., is a liquid pentane of which approximately two-thirds is isopentane and one-third *n*-pentane. Simultaneously, however, some hexanes and heptanes were also formed. The yield of products depended upon the proportion of reactants, varying from 7.2 per cent (result of reaction of a mixture of 4.7 per cent ethylene and 95.3 per cent propane) to 11.2 per cent (from olefin and paraffin, 8.9 and 91.1 per cent, respectively). Isobutane and the unsaturated hydrocarbon, at the temperature and pressure mentioned above, gave mainly 2,2-dimethylbutane and 2-methylheptane, together with some heptanes and octanes. It was also observed that the extent to which alkylation occurred was greater at high pressures (4500-4700 lbs.) than lower pressures (2500 lbs.) though the composition of the resulting liquids was but little affected. Frey and Hepp point out that the rate at which a tertiary hydrogen is replaced by an ethyl radical is greater than for a secondary hydrogen and much more rapid than for a primary hydrogen.

CONDENSATION OF OLEFINS WITH NAPHTHENES

The products from cyclohexane and ethylene would accordingly be mono- and higher ethylcyclohexanes. However, because of a rearrangement of ethylcyclohexanes, described by Grignard and Stratford[46] as occurring in the presence of aluminum chloride, *m*-dimethyl- and 1,2,4,5-tetramethylcyclohexane were actually obtained. These two substances were separated by dehydrogenation over a nickel-alumina catalyst and subsequent bromination. 2,4,5,6-Tetrabromo-1,3-dimethylbenzene so prepared melted at 243°C. The tetramethyl derivative was isolated and identified as the dibromide of the corresponding aromatic compound. Alkylation was believed to take place as indicated below.





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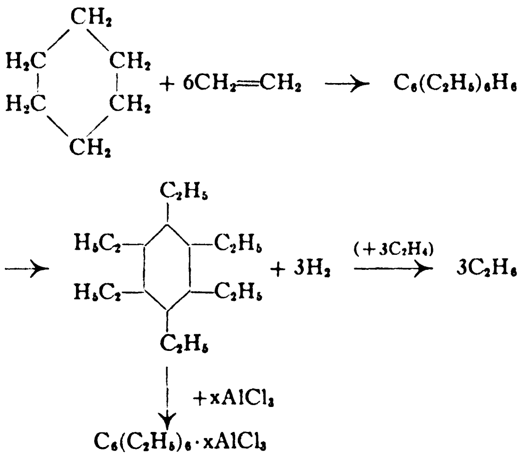
[45] F. E. Frey and H. J. Hepp, *Ind. Eng. Chem.*, 1936, **28**, 1439; *J. Inst. Pet. Tech.*, 1937, **23**, 66A; *Chem. Abs.*, 1937, **31**, 1004.

[46] V. Grignard and R. Stratford, *Compt. rend.*, 1924, 178, 2149; *Chem. Abs.*, 1924, **18**, 3110; *J.S.C.I.*, 1924, **43**, 661B. R. Stratford, *Ann. combustibles liquides*, 1929, 4, 93, 317; *Chem. Abs.*, 1929, **23**, 5564.

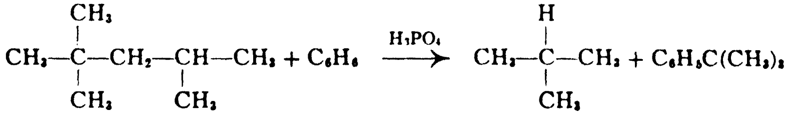
From the pasty reaction mass remaining after distillation of the volatile portion, it was possible to isolate a hydrocarbon (m.p. 147°C.) which was identified as hexaethylbenzene. This was assumed to be formed by intramolecular dehydrogenation of hexaethylcyclohexane. The hydrogen thus liberated was apparently taken up by ethylene since a small amount of ethane was found in the exit gases. This series of reactions may be represented by:



The molecular addition product of the benzene derivative and aluminum is known as a Gustavson complex.[47]

The interaction which takes place between cyclopropane and an aromatic hydrocarbon has been mentioned previously in this chapter. Grosse and Ipatieff[48] have also described an analogous combination between cyclopropane and isobutane in the presence of aluminum and hydrogen chlorides either at room temperature or at —30°C. At the lower temperature some cyclopropane remains unreacted. The product, however, consists largely of various heptanes.

In Chapter 6 the action of aluminum chloride on paraffins and aromatics at high temperatures has been discussed. In this reaction, which is called destructive alkylation, there is cracking of the paraffin and alkylation of the aromatic hydrocarbon. Ipatieff, Komarewsky and Pines[49] have observed that a similar reaction occurs when benzene is heated with either *n*-hexane or 2,2,4-trimethylpentane in the presence of phosphoric acid as a catalyst. In the latter instance alkylation of the aromatic hydrocarbon by olefins formed from the paraffin by action of phosphoric acid is believed to occur.



$$CH_3—\overset{CH_3}{\underset{CH_3}{C}}—CH_2—\underset{CH_3}{CH}—CH_3 + C_6H_6 \xrightarrow{H_3PO_4} CH_3—\overset{H}{\underset{CH_3}{C}}—CH_3 + C_6H_5C(CH_3)_3$$

$$2CH_3(CH_2)_4CH_3 + 2C_6H_6 \xrightarrow{H_3PO_4} C_3H_8 + C_2H_6 + C_6H_5CH(CH_3)_2 + C_6H_5—C_4H_9$$

The results of experiments on alkylation as well as the effect of heating any one of the hydrocarbons either alone or with phosphoric acid are given in Table 128.

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[47] Cf. G. Gustavson. *Compt. rend.*, 1903, **136**, 1065; *J.C.S.*, 1903, (1) **84**, 470. *J. prakt. Chem.*, 1903, (2) **68**, 209; *J.C.S.*, 1903, (1) **84**, 470.

[48] A. V. Grosse and V. N. Ipatieff, Organic Division, American Chemical Society Meeting, Pittsburgh, Sept. 7-10, 1936.

[49] V. N. Ipatieff, V. I. Komarewsky and H. Pines, *J.A.C.S.*, 1936, **58**, 918; *Brit. Chem. Abs.* **A**, 1936, 976; *J. Inst. Pet. Tech.*, 1936, **22**, 395A; *Chem. Abs.*, 1936, **30**, 5191.

TABLE 128.—*The Destructive Alkylation of Hydrocarbons.*

Experiment[a]	1	2	3	4	5	6	7	8	9
Paraffin (grams)	52.0	48.0	50.0	60.0	60.0	30.0	30.0	—	—
Benzene (grams)	51.5	47.5	50.0	—	—	—	—	50.0	50.0
100 Per cent phosphoric acid (grams)	15.0	21.0	—	17.0	—	10.0	—	15.0	—
Reaction time (hours)	6	10	6	6	6	6	6	6	6
Final pressure, atm., at 21°C.	18	19	4	5	4.5	3.0	3.0	0	0
Gases on N-free basis in cc.	7000	6200	1270	2500	2200	1400	1000	100	100
Per Cent Composition of Gases									
H_2	8.1	28.0	10.0	33.5	35.0	22.5	21.7		
CH_4	24.0	—	—	21.0	20.0	—	—		
C_2H_6	—	54.0	—	—	—	—	—		
C_3H_8	4.7	18.0	—	—	—	—		Not analyzed	
i-C_4H_8	—	—	24.0	—	—	—			
n-C_4H_{10}	—	—	—	12.0	13.0	—			
i-C_4H_{10}	63.2	—	65.0	33.5	32.0	—			
Paraffin	—	—	—	—	—	75.0[b]	74.0[c]		
Olefins	—	—	—	—	—	2.5	3.0		
Liquid product from H_3PO_4	85.0	80.0	92.0	44.0	47.0	26.5	27.0	48.0	48.0

[a] In Experiments 2, 6 and 7 the paraffin was *n*-hexane, in 1, 3, 4 and 5 it was 2,2,4-trimethylpentane, in 8 and 9 no paraffin was used. The capacity of the autoclave in which the reaction was carried out was 850 cc. The temperature was 450°C.

[b] Average molecular weight for paraffin was 30.

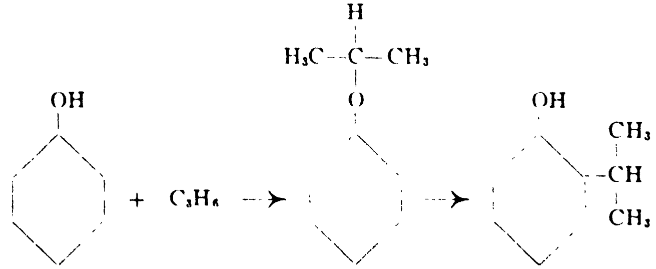
[c] Average molecular weight for paraffin was 34.

In Experiments 1 and 2 the liquid product contained *ter*-butyl- and isopropyl- benzene, respectively; in the others it was largely the original hydrocarbon. The results given above show that there is a destructive alkylation which takes place in the presence of phosphoric acid, but not at all in the absence of a catalyst. There is apparently only slight cracking of the paraffin induced by the acid, since the gaseous products do not differ greatly whether the hydrocarbon is heated alone or with the catalyst.

Another catalyst which has been used to effect the condensation of ethylene with a naphthenic hydrocarbon oil is molybdenum oxide.[50] The product may be employed as a motor fuel.

CONDENSATION OF OLEFINS WITH PHENOLS

The condensation of alkenes with phenols is similar in some respects to that with aromatic hydrocarbons. Reaction is catalyzed by anhydrous metallic halides, sulphuric acid, phosphoric acid and certain activated clays or bleaching earths. Sowa, Hinton and Nieuwland[51] suggested that interaction, with propene, for example, takes place in the following manner:



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[50] M. P. Appleby, C. Cockram, British P. 415,792, 1934, to Imperial Chemical Industries, Ltd.; *J. Inst. Pet. Tech.*, 1934, **20**, 581A; *Chem. Abs.*, 1935, **29**, 918; *Brit. Chem. Abs.* **B**, 1934, 952. French P. 768,166, 1934, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1935, **29**, 580.

[51] F. J. Sowa, H. D. Hinton and J. A. Nieuwland, *J.A.C.S.*, 1932, **54**, 3694; *Brit. Chem. Abs.* **A**, 1932, 1125; *Chem. Abs.*, 1932, **26**, 5294.

The rearrangement (indicated above) of the intermediate compound was studied more extensively by the same workers[52] and was confirmed for several phenyl and cresyl ethers. It is comparable to the shifting of the acyl group of a phenyl ester to form a hydroxy phenyl ketone which occurs on treating the ester with aluminum chloride below 75°C.[53]

One of the most important catalytic agents for the alkylation of phenols is sulphuric acid. Thus, Evans and Edlund[54] observed that a tertiary olefin will react with phenol at 25°C. in the presence of sulphuric acid. A germicidal product has been prepared by the condensation of a phenol and a cracked gasoline fraction in the presence of strong sulphuric acid.[55] The product consists essentially of mixed alkyl phenols in which the side-chains have more than 4 carbon atoms. Compounds synthesized in this manner have been suggested also as antioxidants, particularly for the prevention of gum-formation in gasoline, for the stabilization of lubricating and transformer oils and as anti-aging agents for rubber.[56] Methods for preparing *ter*-amyl phenol[57] have been suggested by Lee and Clark[58] and by Thomas[59] in which phenol is treated with a solution of isopentene in sulphuric acid. Such a procedure is also applicable with an aliphatic or cyclic olefin in 90 per cent or stronger acid. The alkylated product is isolated by diluting the reaction mixture with water. If sulphonation of the phenol has taken place it is necessary to effect hydrolysis of the sulpho group by boiling with dilute acid or distillation with superheated steam.[60] *p-ter*-Amyl phenol is advocated as a plasticizing agent for lacquers containing ethyl cellulose and a compatible phenol-formaldehyde resin.[60a]

Niederl[61] reported the alkylation of polyphenols or their monoethers with diisobutylene in the presence of sulphuric acid. The reactants may be dissolved in acetic acid. The compounds thus secured are 1,1,3,3-tetramethylbutyl derivatives of the hydroxy-compound employed as one of the reacting substances. Although diisobutylene is a mixture of two isomeric trimethylpentenes, only one product is obtained.[62] Interaction, therefore, may be represented as indicated below.

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[52] F. J. Sowa, H. D. Hinton and J. A. Nieuwland, *J.A.C.S.*, 1933, **55**, 3402. 5077; *Brit. Chem. Abs.* **A**, 1933, 1045; *Chem. Abs.*, 1933, **27**, 4785.

[53] See K. W. Rosenmund and W. Schnurr, *Ann.*, 1928, **460**, 56; *Chem. Abs.*, 1928, **22**, 1579; *Brit. Chem. Abs.* **A**, 1928, 1010.

[54] T. Evans and K. R. Edlund, U. S. P. 2,051,473, Aug. 18, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 6761. Canadian P. 353,688, 1935; *Chem. Abs.*, 1936, **30**, 2202

[55] H. E. Buc and R. Schuler, U. S. P. 2,045,749, June 30, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 5777.

[56] D. R. Stevens and W. A. Gruse, U. S. P. 2,061,111, Nov. 17, 1936, to Gulf Oil Corp.; *Chem. Abs.*, 1937, **31**, 845. *Cf.* D. R. Stevens and W. A. Gruse, U. S. P. 2,017,610, Sept. 15, 1935, to Gulf Refining Co.; *Brit. Chem. Abs.* **B**, 1936, 1080; *Chem. Abs.*, 1935, **29**, 8313. *Cf.* C. P. Wilson, Jr., U. S. P. 2,069,294, Feb. 3, 1937; *Chem. Abs.*, 1937, **31**, 1998. W. M. Malisoff and F. G. Hess, U. S. P. 2,061,533, Nov. 24, 1936; *Chem. Abs.*, 1937, **31**, 842. J. P. Smoots, U. S. P. 2,070,978, Feb. 16, 1937, to Standard Oil Co. of Ohio.

[57] See E. Klarmann, U. S. P. 1,953,413, April 3, 1934, to Lehn and Fink, Inc.; *Chem. Abs.*, 1934, **28**, 3842; *Brit. Chem. Abs.* **B**, 1935, 174.

[58] W. M. Lee and L. H. Clark, U. S. P. 2,050,188, Aug. 4, 1936, to Sharples Solvents Corp.; *Chem. Abs.*, 1936, **30**, 6761.

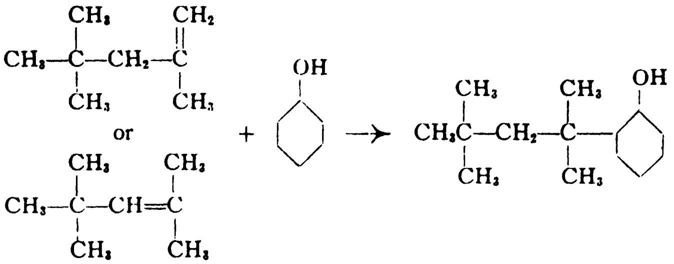
[59] C. A. Thomas, British P. 420,636, 1934, to Sharples Solvent Corp.; *Chem. Abs.*, 1935, **29**, 3351; *J. Inst. Pet. Tech.*, 1935, **21**, 101A.

[60] H. E. Buc, U. S. P. 1,954,985, April 17, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1934, **28**, 3741. British P. 398,218, 1933; *Chem. Abs.*, 1934, **28**, 1358; *Brit. Chem. Abs.* **B**, 1933, 956. French P. 737,556, 1932; *Chem. Abs.*, 1933, **27**, 731. See also H. E. Buc and R. Schuler, U. S. P. 1,948,287, Feb. 20, 1934, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1934, 1095; *Chem. Abs.*, 1934, **28**, 2852

[60a] R. T. Ubben, U. S. P. 2,075,376, Mar. 30, 1937, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, **31**, 3718.

[61] J. B. Niederl, U. S. P. 2,008,032, July 16, 1935, to Röhm & Haas Co.; *Chem. Abs.*, 1935, **29**, 5994. British P. 409,111, 1934; *Chem. Abs.*, 1934, **28**, 6158; *Brit. Chem. Abs.* **B**, 1934, 535. German P. 616,786, 1935; *Chem. Abs.*, 1936, **30**, 735. British P. 431,487, 1934; *Brit. Chem. Abs.* **B**, 1935, 841; *Chem. Abs.*, 1935, **29**, 8239. See also, J. D. Robinson and W. F. Hester, U. S. P. 2,008,337, July 16, 1935, to Röhm & Haas Co.; *Chem. Abs.*, 1935, **29**, 5996; *Brit. Chem. Abs.* **B**, 1936, 1143.

[62] W. F. Hester, U. S. P. 2,008,017, July 16, 1935, to Röhm & Haas Co.; *Chem. Abs.*, 1935, **29**, 5862; *Brit. Chem. Abs.* **B**, 1936, 1143.



Triisobutylene may be substituted for the dimer.[63] In this instance, however, since the former material contains many isomers, of which five have been isolated, it is better to separate it into several fractions and react these individually with phenolic bodies. The polymeric isobutene derivatives so prepared are said to be applicable as antiseptic, fungicidal or bactericidal agents, as intermediates in the manufacture of dyes or as artificial tanning or wetting-out compounds.[64] Bruson and Covert[65] suggest that these substances be hydrogenated to the corresponding hydroxy cycloparaffins. The latter, because of their low boiling points and vapor pressures, are recommended as plasticizers for coating and molding compositions and as lubricants for textile fibers or fine mechanisms, e.g., watches. They may also be oxidized with nitric acid to *ter*-alkyl adipic acids.

Ipatieff[66] proposed that combination between phenols or polyphenols and olefins (such as ethylene or propene) be carried out employing phosphoric acid as the contact agent. Chichibabin[67] observed that the methyl ether of a cresol, such as *p*-methoxy toluene, will react with isobutene in the presence of either phosphoric or sulphuric acid. On the other hand, Vonderwahl[68] has suggested the preparation of 4-*ter*-butyl-3-methyl-phenyl methyl ether by reacting *m*-tolyl methyl ether with isobutene using anhydrous aluminum, zinc, ferric or antimony chloride as the catalyst. Another halide which has been employed in the alkylation of phenols is boron trifluoride. For example, heating tar phenol, ethylene, boron fluoride and hydrogen chloride in an autoclave is said to form the phenol ethyl ether.[69]

Various other substances such as alumina, aluminum phosphate, mixed aluminum and magnesium silicates, and kieselguhr as well as zinc chloride have been suggested as catalysts for the preparation of isopropylcresols from propene and the methyl phenol.[70] The reaction may be carried out in liquid or vapor phase. In this way it was found possible to make thymol (3-hydroxy-4-isopropyltoluene) and its isomers, including 4-hydroxy-2-isopropyltoluene (m.p. 37°C.) and 3-hydroxy-2-isopropyltoluene (m.p. 69°C.). Siliceous catalysts, such as fuller's earth or clay, have been employed by Britton and Perkins[71] to effect the condensation of a phenol and cyclohexene at 100° to 350°C., and 1 atmosphere pressure, to cyclohexylphenol.

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[63] W. F. Hester, U. S. P. 2,060,573, Nov. 10, 1936, to Röhm & Haas Co.; *Chem. Abs.*, 1937, **31**, 507.

[64] Halogenated or sulphonated derivatives of diisobutylene and phenols are suggested for the same purposes: British P. 452,335, 1936, to Monsanto Chemical Co.; *Chem. Abs.*, 1937, **31**, 485.

[65] H. A. Bruson and L. W. Covert, U. S. P. 2,026,668, Jan. 7, 1936, to Röhm & Haas Co.; *Chem. Abs.*, 1936, **30**, 1065.

[66] V. N. Ipatieff, U. S. P. 2,046,900, July 7, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 5592.

[67] A. E. Chichibabin, U. S. P. 1,933,775, Nov. 7, 1933, to Schering-Kahlbaum A.-G.; *Chem. Abs.*, 1934, **28**, 487. See also A. E. Chichibabin, *Compt. rend.*, 1934, **198**, 1239; *Brit. Chem. Abs.* **A**, 1934, 646; *Chem. Abs.*, 1934, **28**, 3722.

[68] E. Vonderwahl, U. S. P. 1,927,053, Sept. 19, 1933, to Givaudan-Delawanna, Inc.; *Brit. Chem. Abs.* **B**, 1934, 751; *Chem. Abs.*, 1933, **27**, 5752.

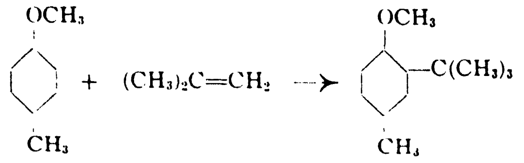
[69] L. Hofmann and C. Wulff, German P. 604,867, 1934; *Chem. Abs.*, 1935, **29**, 814.

[70] K. Schöllkopf, German P. 586,150, 1933, to Rheinische Kampfer-Fabrik G.m.b.H.; *Chem. Abs.*, 1934, **28**, 483.

[71] E. C. Britton and R. P. Perkins, U. S. P. 1,917,823, July 11, 1933, to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1934, 394; *Chem. Abs.*, 1933, **27**, 4541.

In an analogous manner, Schoeller and Jordan[72] reacted a phenol and propene at 135 to 200°C.

Alkylation of phenyl ethers has been accomplished by Dubinin[73] using 5 per cent of aluminum chloride dissolved in the ether as a catalyst. For example, isobutene and *p*-methoxytoluene furnished 1-methyl-4-methoxy-3-*ter*-butylbenzene.



The quantity of product obtained corresponded to a 71 per cent yield. The *ter*-butyl derivative of *o*-methoxytoluene was also synthesized in like manner, the yield in this instance amounting to 58 per cent. The product from 1,3-dimethoxybenzene (b.p. 120-122°C. at 11 mm.) was also made in a 71 per cent yield and was shown to be probably 4-*ter*-butyl-1,3-dimethoxybenzene, together with some 4,6-di-*ter*-butyl-1,3-dimethoxybenzene.

The interaction of 3-methylpentene with phenolic substances leads, according to Koenigs and Carl,[74] to the formation of alkylated derivatives. For example, 4-*ter*-amyl-2-methyl-6-isopropylphenol was obtained from thymol and isoamylene. A similar reaction could be carried out using styrene (phenylethylene) and a phenol, the product being, in this case, a hydrated stilbene.

An extension of this condensation applies to the addition of alcohols[75] or glycols[76] to olefins with the formation of *ter*-alkyl ethers. The reaction is catalyzed by sulphuric, phosphoric or aromatic sulphonic acids, metallic chlorides, for example, those of zinc, aluminum, or iron, or non-metallic halides, e.g., boron trifluoride or phosphorus oxychloride. Other substances which exert an accelerating effect are charcoal, kaolin, silica gel or kieselguhr. As an example,[77] methyl sulphuric acid (from the corresponding alcohol and acid and containing 55 per cent free acid) was treated for 2 hours at 95 to 100°C. with a butane-butene fraction (95 per cent olefin) of cracking gas. The mixture was cooled and allowed to stratify. The

TABLE 129. - *Synthetic Ethers of Type ROR_1.*

Alkyl Groups		Boiling	
R	R_1	Point, °C.	d_4^{20}
Methyl	*ter*-Butyl	55	0.7405
Ethyl	*ter*-Butyl	73	0.7404
Isopropyl	*ter*-Butyl	87-88	0.742
n-Butyl	*ter*-Butyl	123-124	0.7615
Isobutyl	*ter*-Butyl	114	0.7516
sec-Butyl	*ter*-Butyl	114-115	0.7604
Isoamyl	*ter*-Butyl	138-140	0.7662
Methyl	*ter*-Amyl	86-87	0.7703
Ethyl	*ter*-Amyl	101-102	0.7657
Isopropyl	*ter*-Amyl	114-115	—
Methyl	*ter*-Hexyl	113	0.7815

[72] W. Schoeller and H. Jordan, U. S. P. 2,054,270, Sept. 15, 1936, to Schering-Kahlbaum A.-G.; *Chem. Abs.*, 1936, **30**, 7583.

[73] B. M. Dubinin, *Compt. rend. acad. sci. U.R.S.S.* [*N.S.*], 1935, **3**, 263; *Chem. Abs.*, 1936, **30**, 1370.

[74] W. Koenigs and R. W. Carl, *Ber.*, 1891, **24**, 3889; *J.C.S.*, 1892, **62**, 446; *Chem. Zentr.*, 1892, **1**, 287.

[75] T. W. Evans and K. R. Edlund, *Ind. Eng. Chem.*, 1936, **28**, 1186; *Brit. Chem. Abs.* **A**, 1936, 1486. U. S. P. 1,968,601, July 31, 1934, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 5831; *Brit. Chem. Abs.* **B**, 1935, 619. Canadian P. 352,811, 1935; *Chem. Abs.*, 1935, **29**, 8001.

[76] See Chapter 22.

[77] T. W. Evans and E. F. Bullard, U. S. P. 2,067,385, Jan. 12, 1937, to Shell Development Co.

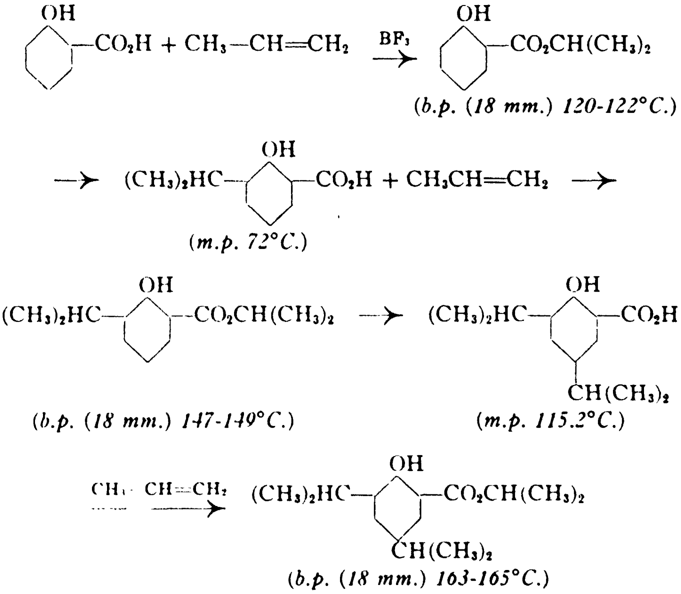
upper layer was then distilled, in the presence of alkali, to recover methyl-*sec*-butyl ether (boiling at 61°C.). The lower layer was diluted with methyl alcohol and subjected to the action of butene.

A softening agent for cellulose esters may be obtained by heating isopropanol with isobutene and concentrated sulphuric acid.[77a] When interaction is carried out at 95°C., isopropyl-*ter*-butyl ether is formed. Similar compounds, applicable for the same use, may be secured by treatment of other alcohols with olefins, provided the latter are capable of yielding tertiary alcohols when hydrated.

A number of ethers synthesized from olefins and alcohols are listed in Table 129.

CONDENSATION OF OLEFINS WITH ACIDS

Direct union of olefins and carboxylic acids to give esters has been previously discussed.[78] However, those reactions involving hydroxy aromatic acids are considered here since in many respects they resemble interaction between unsaturated hydrocarbons and phenols. Croxall, Sowa and Nieuwland[79] studied alkylation of salicylic acid with propene in the presence of boron trifluoride. The products were 3-mono- and 3,5-di-isopropyl-2-hydroxy-benzoic acids, their isopropyl esters and isopropyl salicylate. Combination was considered to take place with the formation of isopropyl salicylate, which underwent rearrangement followed by esterification and further reactions.



Propene (under a pressure of 8 to 10 cm. of mercury) was conducted into a suspension of 35 g. of salicylic acid in 210 g. of heptane with which 4 g. of boron trifluoride had been incorporated. A few grams more of boron fluoride were added during the reaction. After three days 1.25 moles of propene had been absorbed. The reaction was then stopped and the products mentioned above isolated. No alkoxylated derivatives were observed which was thought to be due to the greater

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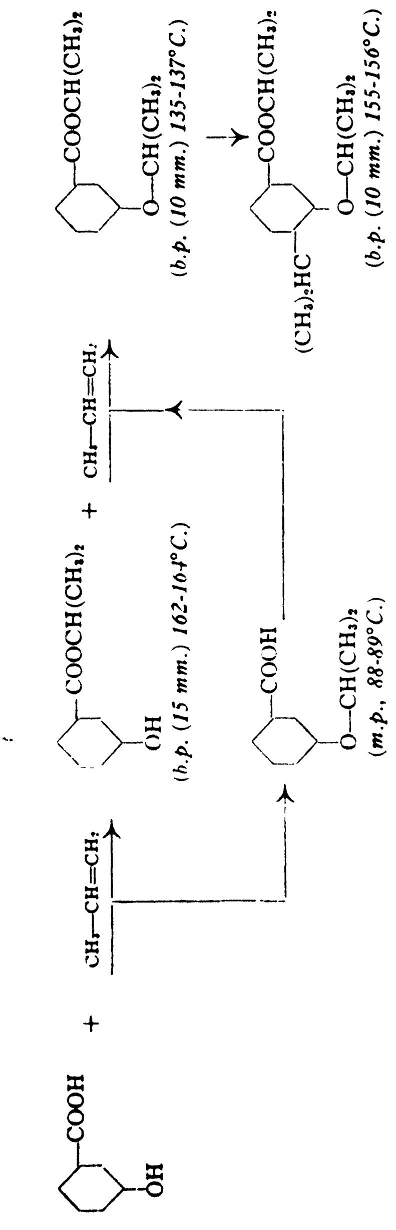
[77a] German P. 629,601, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 6195.

[78] See Chapter 12.

[79] W. J. Croxall, F. J. Sowa and J. A. Nieuwland, *J.A.C.S.*, 1934, **56**, 2054; *Chem. Abs.*, 1935, **29**, 148; *Brit. Chem. Abs.* **A**, 1934, 1349.


COOH
OH
+
CH₃—CH=CH₂
COOCH(CH₃)₂
OH
(b.p. (15 mm.) 162-164°C.)
+
CH₃—CH=CH₂
COOCH(CH₃)₂
O—CH(CH₃)₂
(b.p. (10 mm.) 135-137°C.)
COOH
O—CH(CH₃)₂
(m.p., 88-89°C.)
COOCH(CH₃)₂
(CH₃)₂HC
O—CH(CH₃)₂
(b.p. (10 mm.) 155-156°C.)

tendency of boron trifluoride to condense with the carboxy or carbalkoxy group than the phenolic group. The postulated mechanism of rearrangement was supported by isomerization of isopropyl salicylate under the experimental conditions employed.

In addition to the reaction of propene with *o*-hydroxybenzoic acid, those with *m*- and *p*-hydroxybenzoic acids have also been investigated.[80] In the latter instances, isopropyl ethers of hydroxybenzoic and hydroxyisopropylbenzoic acid and their esters were isolated. It was suggested that the formation of 3-isopropoxybenzoic acid and isopropyl *m*-hydroxy benzoate occurred simultaneously, whereas 4-isopropoxybenzoic acid was formed to the exclusion of isopropyl *p*-hydroxy benzoate. Interactions occurring when *m*-hydroxybenzoic acid was used are indicated on page 608.

The mechanism of the intermediate step was not completely established, for both isopropyl *m*-hydroxy benzoate and 3-isopropoxybenzoic acid rearranged to give the same product (3-hydroxy-4-isopropylbenzoic acid; m.p. 138-140°C.) under the experimental conditions.

Reaction between *p*-hydroxybenzoic acid and propene may be represented by the equations given on page 610.

The exact sequence of steps is uncertain, because of three possible courses for the reaction, viz., rearrangement of either isopropyl group or direct alkylation of the ring. It was considered that migration of the oxyisopropyl group was most probable since *p*-isopropoxybenzoic acid rearranges for the most part to 4-hydroxy-3-isopropylbenzoic acid.

CONDENSATION OF ALKENES WITH ACID HALIDES

Addition of acid chlorides to unsaturated hydrocarbons is a fairly general reaction which has prompted study by many investigators.[81] The reaction occurs, for example, with chlorosulphonic acid which unites with aryl ethylenes, e.g., styrene, safrole, coumarone and indene, to give chlorosulphonic acids in which the chlorine may be replaced by other groups, such as hydroxyl.[82] Phosgene, which may be considered either as the chloride of chloroformic acid or the dichloride of carbonic acid, is said to combine with ethylene in some solvents. Varshavskii and Doroganyevskaya[83] have shown that no 2-chloropropionyl chloride is formed in the presence of aluminum chloride when either toluene or carbon tetrachloride is the liquid medium. In the former, however, reaction tended toward that of the conventional Friedel-Crafts type. On the other hand, with carbon tetrachloride as a solvent the product apparently consisted of polymers formed by the action of aluminum chloride on the olefin. These results were corroborated by Klebanskii and Chevuichalova,[84] who observed, furthermore, that chlorobenzene was also unsatisfactory as a solvent. The optimum conditions were found to be cooling and stirring of a solution of 0.5 g. aluminum chloride per mole of carbon disulphide in which phosgene and ethylene reacted. The main product was believed to be 2-chloropropionyl chloride, although this substance could not be isolated directly. The reaction mixture was decomposed by addition of absolute alcohol, and the esters of chloro-

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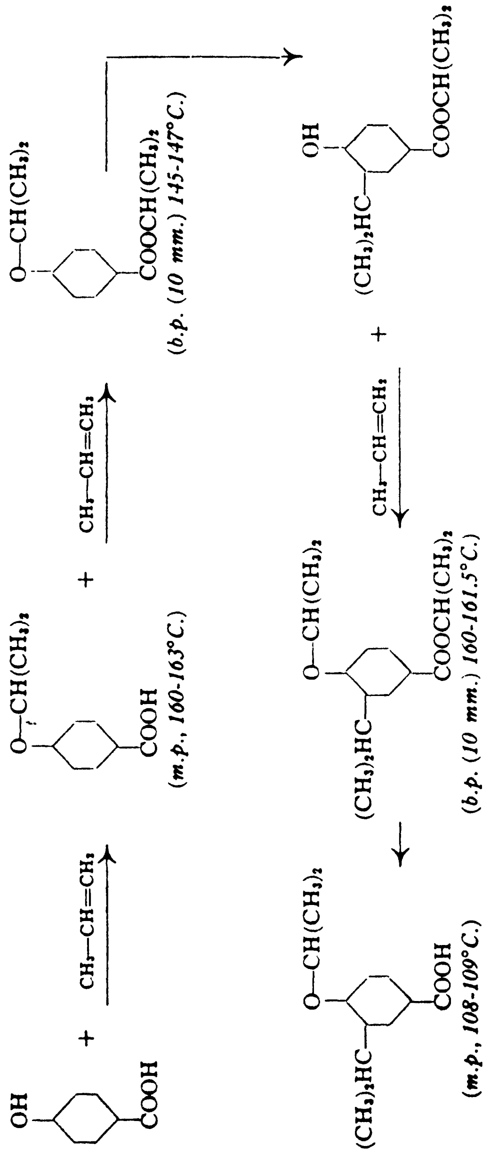
[80] W. J. Croxall, F. J. Sowa and J. A. Nieuwland, *J.A.C.S.*, 1935, 57, 1549; *Brit. Chem. Abs.* **A**, 1935, 1358; *Chem. Abs.*, 1935, 29, 7296.

[81] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[82] French P. 780,027, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 5864.

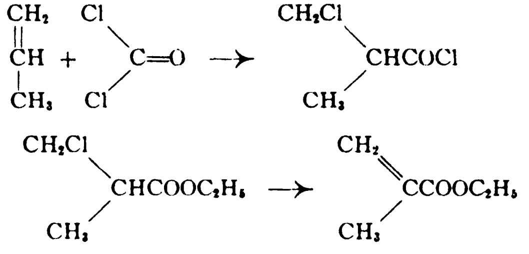
[83] S. L. Varshavskii and E. A. Doroganyevskaya, *Gazz. chim. ital.*, 1934, 64, 53; *Brit. Chem. Abs* **A**, 1934, 508; *Chem. Abs.*, 1934, 28, 5043.

[84] A. L. Klebanskii and K. K. Chevuichalova, *J. Gen. Chem.* (*U.S.S.R.*), 1935, 5, 535; *Chem. Abs.*, 1935, 29, 6879. *Compt. rend. acad. sci. U.R.S.S.*, 1935, 2, 42; *Brit. Chem. Abs.* **A**, 1935, 845; *Chem. Abs.*, 1935, 29, 5814.

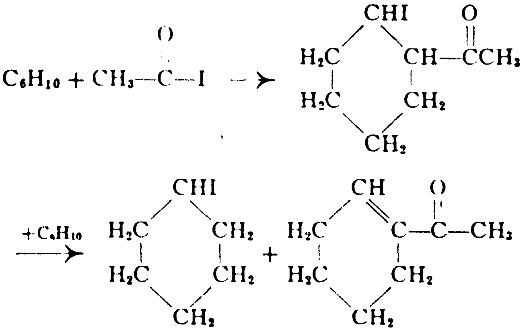

OH
COOH
+
CH₃—CH=CH₂
O—CH(CH₃)₂
COOH
(m.p., 160-163°C.)
+
CH₃—CH=CH₂
O—CH(CH₃)₂
COOCH(CH₃)₂
(b.p. (10 mm.) 145-147°C.)
OH
(CH₃)₂HC
COOCH(CH₃)₂
+
CH₃—CH=CH₂
O—CH(CH₃)₂
(CH₃)₂HC
COOCH(CH₃)₂
(b.p. (10 mm.) 160-161.5°C.)
O—CH(CH₃)₂
(CH₃)₂HC
COOH
(m.p., 108-109°C.)

propionic acid then separated from polymerized ethylene. No better results were obtained when zinc chloride was used in place of aluminum chloride.

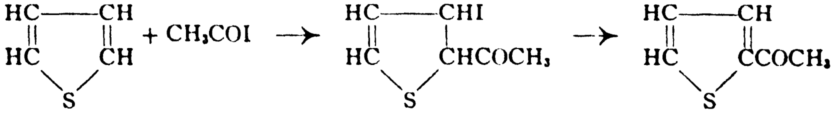
Reid[85] also interacts phosgene, in the presence of aluminum chloride, with propene to give a β-chloro acid chloride. Esters are then formed by the addition of an alcohol such as ethanol, propanol, ethanediol or propantriol. By removal of hydrogen chloride from the latter, esters of methacrylic acid are obtained.



Combination of chlorides of aliphatic organic acids with ethylenic compounds should lead to the synthesis of 2-chloroketones. Frolich and Wiezevich[86] have made chloroethyl methyl ketone from ethylene and acetyl chloride by heating them to a temperature of at least 100°C. under pressure in the presence of charcoal. Stevens[87] has studied the action of acetyl iodide on unsaturated hydrocarbons. He observed that the 2-iodoketones formed were very reactive and lost hydrogen iodide readily. For example, cyclohexene and acetyl iodide gave iodohexahydroacetophenone which then yielded tetrahydroacetophenone and cyclohexyl iodide.[88]



When thiophene was treated with the acid iodide some acetothienone[89] was isolated from the reaction product. Its formation can be indicated by:



In addition large quantities of iodine and tarry material were obtained. These are probably due to loss of iodine from a diiodo derivative and polymerization of the resulting diketone. Divinyl ether and furan also reacted vigorously with acetyl iodide.

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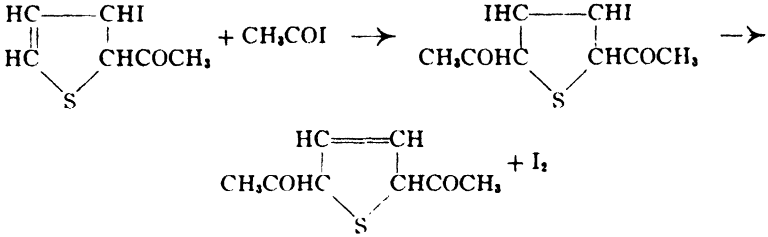
[85] E. E. Reid, U. S. P. 2,028,012, Jan. 14, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 1387.

[86] P. K. Frolich and P. J. Wiezevich, U. S. P. 2,006,198, June 25, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 5457; *Brit. Chem. Abs.* **B**, 1936, 824.

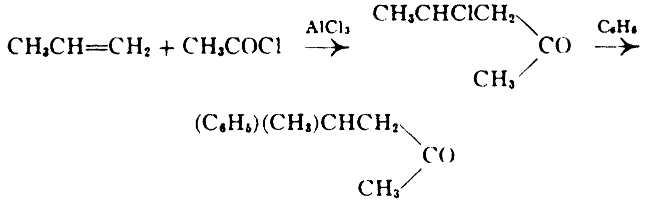
[87] P. G. Stevens, *J.A.C.S.*, 1934, **56**, 450; *Chem. Abs.*, 1934, **28**, 1661; *Brit. Chem. Abs.* **A**, 1934, 391.

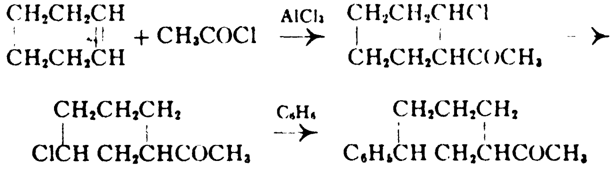
[88] *Cf.* the results of E. L. Gustus and P. G. Stevens (*J.A.C.S.*, 1933, **55**, 378; *Chem. Abs.*, 1933, **27**, 956) who report that aliphatic ethers react with acetyl iodide to give an addition compound which in turn decomposes to an alkyl iodide and alkyl acetate.

[89] This compound may be prepared also from thiophene and acetyl chloride. G. Stadnikoff and W. Rodowsky, *Ber.*, 1928, **61**, 268; *Chem. Abs.*, 1928, **22**, 1774; *Brit. Chem. Abs.* **B**, 1928, 427.



The condensation of acetyl chlorides with cyclohexene, cyclopentene, cyclohexene carboxylic acid, ethylene, propene, butene-1 and butene-2, and hept-3-en-2-one has been studied by Nenitzescu and Gavat.[90] It was found that in the presence of aluminum chloride the reaction led to the formation of a chloroketone in which the chlorine atom had migrated to a remote carbon atom of the condensation product. However, the wandering would not go so far as a terminal methyl group. Thus, cyclohexene gave 4-chlorohexahydroacetophenone, and propene and acetyl chloride, followed by treatment with benzene, gave 2-phenylpentanone-4.



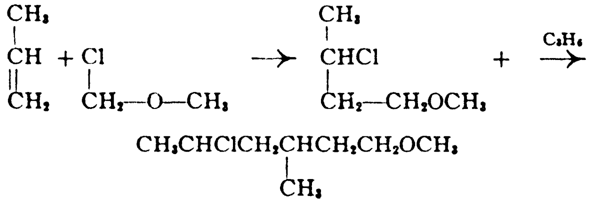


The reactions were carried out using carbon disulphide as a liquid medium. For example, 30 liters of butene-1 (gas) were slowly introduced into a solution of 133 g. aluminum chloride and 78 g. acetyl chloride in 150 cc. carbon disulphide maintained at —14°C. After two layers had separated, the upper was removed and added to 300 cc. of benzene and 30 g. aluminum chloride. The mixture was refluxed at 40°C. for 4 hours and the product (identified as 5-phenylhexanone-2, b.p. 122-125°C. at 9 mm.) separated by distillation. The yield was 19 g. The results obtained in these experiments showed that the migration of the chlorine atom was fairly general. With alkenes having more than 4 carbon atoms in a chain, there was so much polymerization under the experimental conditions that the resulting ketones could not be isolated. Those of higher molecular weights (such as 6-phenylheptanone-2) were made by condensation of the corresponding alk-3-en-2-ones (from an aldehyde and acetone) with benzene. Rearrangement of the phenyl group was shown to take place by synthesizing 5-phenylhexanoic acid and passing this (with acetic acid) over thorium oxide at 400°C. The resulting ketone (6-phenylheptanone-2) was identical with that previously mentioned.

[90] C. D. Nenitzescu and I. Gavat, *Ann.*, 1935, 519, 260; *Chem. Abs.*, 1935, 29, 7279; *Brit. Chem. Abs.* A, 1935, 1368.

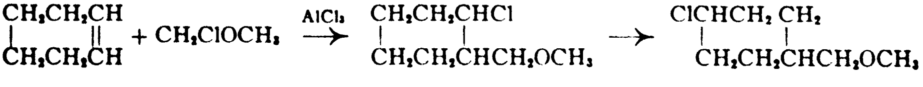
Bergs[91] interacted cyclohexene and phenylacetyl chloride in carbon disulphide solution in the presence of stannic chloride. After treatment of the product with diethyl aniline he obtained 1-phenylacetylcyclohexene-1. Nenitzescu and Cioranescu[92] found that when cyclohexene was the solvent and maintained at low temperatures union between an olefin and an acid chloride proceeded normally to give a chloroketone. However, on raising the temperature, the chlorine atom was eliminated. This was attributed to interaction with hydrogen liberated by intracondensation of solvent molecules, e.g., cyclohexane, to furnish dicyclohexane and hydrogen. As an illustration of this mode of procedure, 68 g. of cyclopentene and 78 g. of acetyl chloride were dissolved in 200 cc. of cyclohexane, and to the solution, maintained at —15°C., were slowly added 266 g. of aluminum chloride. The temperature was then increased to 70°C. and kept there until the evolution of hydrogen chloride ceased. The product in this instance was not methyl-chlorocyclopentyl ketone but methyl cyclopentyl ketone.

Somewhat related to an acid halide, at least insofar as the lability of the halogen atom is concerned, are α-haloethers such as chlorodimethyl ether. Scott[93] observed that these α-halogenated ethers condense with olefinic substances to give γ-haloethers. Reaction is catalyzed by readily hydrolyzable metal halides and may be carried out under increased pressure. For example, chloromethyl ether and propene condense under 150 lbs. per sq. in. at 50 to 70°C. in the presence of bismuth chloride to give methyl 3-chlorobutyl and methyl 5-chloro-3-methylhexyl ethers, the latter as a secondary product.



$$\begin{array}{l} CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{array} + \begin{array}{l} Cl \\ | \\ CH_2{-}O{-}CH_3 \end{array} \longrightarrow \begin{array}{l} CH_3 \\ | \\ CHCl \\ | \\ CH_2{-}CH_2OCH_3 \end{array} + \xrightarrow{C_3H_6} \begin{array}{l} CH_3CHClCH_2CHCH_2CH_2OCH_3 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CH_3 \end{array}$$

Nenitzescu and Przemetzki[94] found that cyclohexene and chloromethyl ether condense in a medium of carbon disulphide, in the presence of zinc chloride, to give 4-chloro-1-methoxymethyl cyclohexene. The 2-chloro derivative was probably formed as an intermediate. This shift of the chlorine atom is in accordance with the theory of migration previously advanced in connection with the addition of acid chlorides to olefin, that is, that the chlorine atom migrates to a remote carbon atom of the condensation product, though not so far as to a terminal methyl group.



$$\begin{array}{l} CH_2CH_2CH \\ | \qquad\quad \| \\ CH_2CH_2CH \end{array} + CH_2ClOCH_3 \xrightarrow{AlCl_3} \begin{array}{l} CH_2CH_2CHCl \\ | \qquad\quad | \\ CH_2CH_2CHCH_2OCH_3 \end{array} \longrightarrow \begin{array}{l} ClCHCH_2\,CH_2 \\ | \qquad\quad | \\ CH_2CH_2CHCH_2OCH_3 \end{array}$$

The structure of the methylmethoxy compound was further substantiated by treating it with benzene to secure 4-phenyl-1-methylmethoxy cyclohexane and dehydrogenating the latter to the corresponding aromatic which in turn was oxidized to *p*-phenylbenzoic acid.

A somewhat analogous reaction to that of olefins and chloroethers is the union of unsaturated hydrocarbons and chlorinated esters. For example, methyl acetate is halogenated and the resulting compound then condensed with ethylene, using aluminum chloride or boron trifluoride as catalyst, to yield the corresponding halogenated ester.[95] Dehalogenation of compounds of the latter type may be accomplished by treatment with hydrogen at 150 to 300°C. and pressures of 100 lbs. per sq. in. or higher.

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[91] H. Bergs, C. Wittfeld and E. Wildt, *Ber.*, 1934, 67, 238; *Brit. Chem. Abs.* A, 1934, 409.

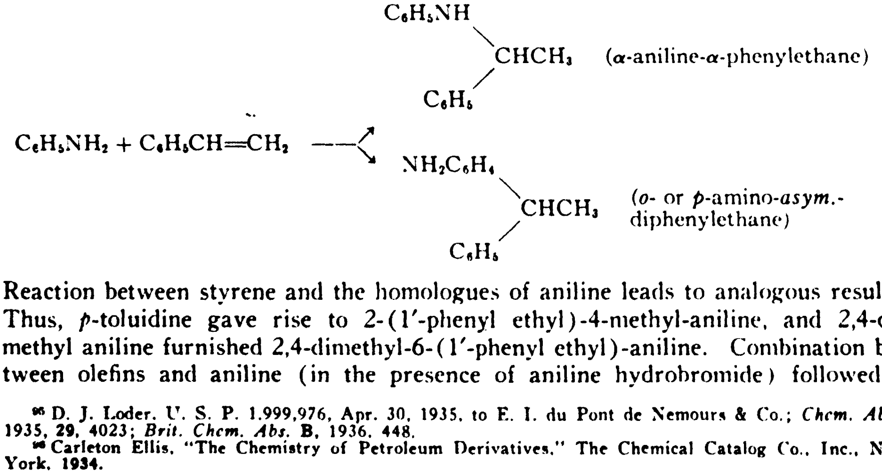
[92] C. D. Nenitzescu and E. Cioranescu, *Ber.*, 1936, 69, 1820; *Chem. Abs.*, 1936, 30, 6712; *Brit. Chem. Abs.* A, 1936, 1379.

[93] N. D. Scott, U. S. P. 2,024,749, Dec. 17, 1935, to E. I. du Pont de Nemours & Co.; *Zentr.*, 1936, 1, 4074; *Chem. Abs.*, 1936, 30, 1067. British P. 423,520, 1935; *Chem. Abs.*, 1935, 29, 4374; *Brit. Chem. Abs.* B, 1935, 297.

[94] C. D. Nenitzescu and V. Przemetzki, *Ber.*, 1936, 69, 2706; *Chem. Abs.*, 1937, 31, 2175.

CONDENSATION OF OLEFINS WITH AMMONIA AND AMINES

Interaction between an olefin and ammonia (or a primary or secondary amine) to give an amine has not received very great attention.[96] According to Sun[97] activation energy calculations indicate that combination will not occur readily and that a primary amine will decompose into a secondary amine rather than into hydrazine and ethylene. Gasoline fractions containing amino bodies may be secured by having ammonia present during cracking operations[98] or by treating the cracked vapors with chlorine and this nitrogen compound under pressure and at temperatures of 150° to 315°C.[99] In place of olefins, substances giving rise to them may be employed in the preparation of secondary amines.[100] For example, an arylamine (e.g., aniline, *o*- or *p*-toluidine) and cyclohexanol are conducted, under pressure and at temperatures of 200° to 270°C., over a non-metallic catalyst. Hydrated silicates, or the oxides of thorium, aluminum or tungsten may be employed. Hickinbottom has investigated the addition of arylamines to alkenes[101] and styrene.[102] There was a tendency in either case for the reaction to give two types of product; (1) a secondary alkyl, or substituted, phenylamine, and (2) a primary substituted arylamine. Thus, from aniline and styrene at 200 to 240°C., using aniline hydrochloride as a catalyst, were obtained α-anilino-α-phenylethane as well as *o*- and *p*-amino-*asym.*-diphenylethane.


C₆H₅NH
CHCH₃
(α-aniline-α-phenylethane)
C₆H₅
C₆H₅NH₂ + C₆H₅CH=CH₂
NH₂C₆H₄
CHCH₃
(o- or p-amino-asym.-diphenylethane)
C₆H₅

Reaction between styrene and the homologues of aniline leads to analogous results. Thus, *p*-toluidine gave rise to 2-(1′-phenyl ethyl)-4-methyl-aniline, and 2,4-dimethyl aniline furnished 2,4-dimethyl-6-(1′-phenyl ethyl)-aniline. Combination between olefins and aniline (in the presence of aniline hydrobromide) followed a somewhat similar course. For example, 6 g. of 2-methylbutene-2, 30 g. of aniline and 3 g. of aniline hydrobromide were heated in sealed tubes at 230 to 250°C. for 6.5 hours. The product was 3.7 g. *p*-amino-*ter*-amylbenzene, 0.57 g. N-*ter*-amylaniline and 2.05 g. diphenylamine. The latter was probably formed directly from the aniline.

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[95] D. J. Loder, U. S. P. 1,999,976, Apr. 30, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 4023; *Brit. Chem. Abs.* **B**, 1936, 448.

[96] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[97] Cheng-E. Sun, *J. Chinese Chem. Soc.*, 1935, **3**, 1; *Chem. Abs.*, 1935, **29**, 4280; *Brit. Chem. Abs.* **A**, 1935, 849.

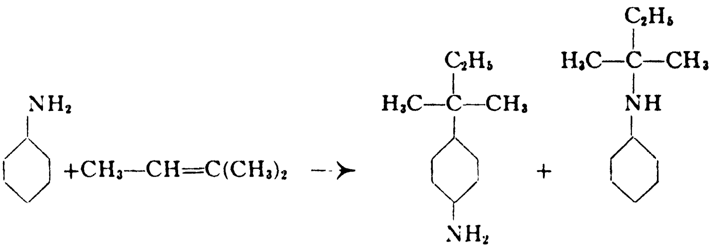
[98] G. Egloff and R. E. Schaad, U. S. P. 1,973,474, Sept. 11, 1934, to Universal Oil Products Co.; *Chem. Abs.*, 1934, **28**, 6997; *Brit. Chem. Abs.* **B**, 1935, 759.

[99] J. C. Morrell and G. Egloff, U. S. P. 2,040,395, May 12, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 4659.

[100] British P. 414,574, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 474; *Brit. Chem. Abs.* **B**, 1934, 873. French P. 765,450, 1934; *Chem. Abs.*, 1934, **28**, 6724. See also British P. 406,700, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1934, 443; *Chem. Abs.*, 1934, **28**, 4745. French P. 747,905, 1933; *Chem. Abs.*, 1933, **27**, 5083. Also British P. 421,596, 1935; *Chem. Abs.*, 1935, **29**, 3687; *Brit. Chem. Abs.* **B**, 1935, 218. P. Herold and K. Smeykal, German P. 631,737, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, **31**, 1428.

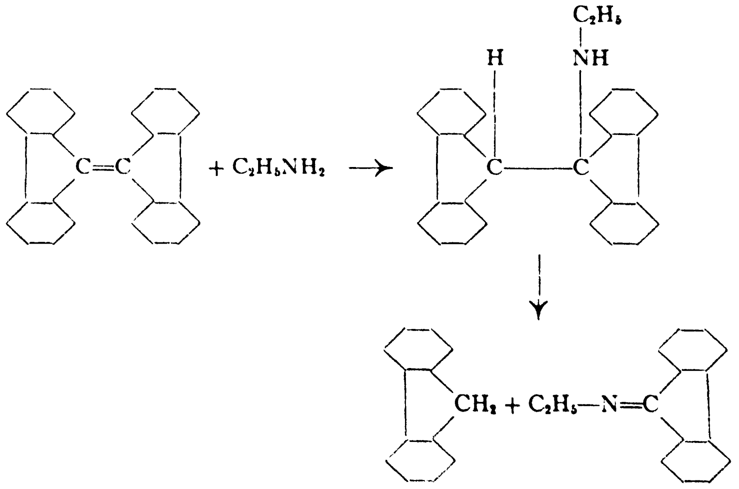
[101] W. J. Hickinbottom, *J. Chem. Soc.*, **1935**, 1279; *Chem. Abs.*, 1935, **29**, 7951; *Brit. Chem. Abs.* **A**, 1935, 1488.

[102] W. J. Hickinbottom, *J. Chem. Soc.*, **1934**, 319; *Chem. Abs.*, 1934, **28**, 3388; *Brit. Chem. Abs.* **A**, 1934, 644.



The formation of an alkyl aniline is favored by lowering the proportion of aniline hydrobromide.[103] Experiments were carried out using 3-methyl- and 3-ethylpentene-2 and octene. It was found that the structure of the olefin played an important part in determining whether amino- or ring-alkylation occurred. Although isoamylene gave a preponderance of the products of the latter type, the reverse was true of octene (from dehydration of *sec*-octanol).

In addition to the investigations of Hickinbottom, the work reported by Pinck and Hilbert[104] on the addition of ammonia and ethylamine to the unsaturated bond of dibiphenylene ethylene deserves mention. It was observed that heating 1 g. of the hydrocarbon and 15 cc. of liquid ammonia in a sealed tube at 65°C. for 3 weeks gave 0.5 g. of an unidentified substance (m.p. 300°C.) and 0.4 g. of 9-iminofluorene. In place of ammonia, methyl-, ethyl and benzylamine were also employed. The main product when ethylamine was one of the reactants was 1-ethylaminodiphenylene ethane. Dissociation of the latter was brought about by heating 2 g. of the substance with 20 c.c. of absolute ethanol for 10 days at 100°C. In addition to fluorene and 9-ethyliminofluorene, some fluorenone was formed, probably due to hydrolysis of the imino derivative.



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[103] For a discussion of the rearrangement of alkyl anilines and their hydrobromides, see W. J. Hickinbottom, *J. Chem. Soc.*, **1934**, 1700; *Brit. Chem. Abs.* **A**, 1935, 76; *Chem. Abs.*, 1935, **29**, 748.

[104] L. A. Pinck and G. E. Hilbert, *J.A.C.S.*, 1935, 57, 2398; *Chem. Abs.*, 1936, **30**, 1779.

Chapter 25

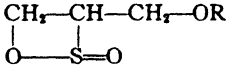
Miscellaneous Reactions of Olefins (II)

The preceding chapter was devoted to a discussion of the miscellaneous reactions of olefins with a number of organic reagents, involving principally condensations with paraffins (the so-called alkylation process), aromatics, phenols, acid chlorides, amines and ammonia. The present chapter will deal with the action of various inorganic substances, such as the oxides and halides of sulphur and nitrogen, carbon monoxide, and metallic salts and of aldehydes on the simpler unsaturated hydrocarbons.

Although most of the reactions involved are of interest only from the standpoint of general properties, several also have attained technical importance, or may hold potential commercial possibilities. One instance of the former is the use of mercuric acetate and thiocyanogen in analytical procedures.[1] The latter type may be represented by the production of acids by the union of carbon monoxide and steam with olefins, or the production of synthetic resins (by condensation of unsaturates with aldehydes) as will be discussed in due course in this chapter.

REACTION OF SULPHUR DIOXIDE AND SULPHITES WITH OLEFINS

Sulphur dioxide and its various derivatives, i.e., sulphurous acid and its salts, combine with olefins under many conditions.[2] Contrary to the results obtained by the action of sulphuric acid (which leads to the formation of sulphates)[3] the products formed from sulphurous acid and sulphites are usually sulphonic acids, or condensed sulphones. One of the earliest reports of the reaction of an olefinic substance and sulphur dioxide was made by Solonina.[4] He found that allyl ethers reacted in benzene solution to give sulphur-containing compounds which he represented by the formula:



Subsequently, the reaction of sulphur dioxide and unsaturated hydrocarbons was investigated by various workers. Thus from this reagent and cyclohexene, Frederick, Cogan and Marvel[5] have isolated a polymolecular sulphone with a molecular weight of about 6000, which they represented by the probable formula:

---

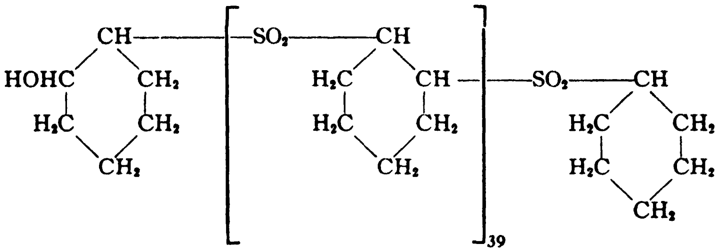
[1] See Chapter 50 of this text. Also, Chapter 25 and 50 of Carleton Ellis. "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co.. Inc.. New York. 1934. For hydrogenation of olefins, consult Carleton Ellis. "Hydrogenation of Organic Substances." D. Van Nostrand Co., New York, 1930.

[2] For example, the formation of disulpho-propionic and butyric acid has been investigated by H. J. Backer and A. E. Beute. *Rec. trav. chim.*, 1935, 54, 601, 621; *Chem. Abs.*, 1936, 30, 3776. 3777; *Brit. Chem. Abs.* A, 1935, 1106, 1107.

[3] See Chapters 14 and 16.

[4] V. Solonina, *J. Russ. Phys.-Chem. Soc.*, 1898, 30, 826; *J.C.S.*, 1899, 76, 681; *Chem. Zentr.*, 1899, 1, 248.

[5] D. S. Frederick, H. D. Cogan, and C. S. Marvel, *J.A.C.S.*, 1934, 56, 1815; *Chem. Abs.*, 1934, 28, 6118; *J. Inst. Pet. Tech.*, 1934, 20, 522A; *Brit. Chem. Abs.* A, 1934, 1095.



This substance was a white amorphous solid which softened and decomposed above 200°C. Although quite soluble in chloroform and tetrachloroethane, it was only slightly soluble in most other solvents. Heating to 250°C. with 90 per cent potassium hydroxide solution caused decomposition, largely to cyclohexene and octahydrobiphenyl.

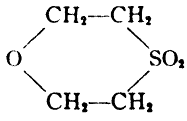
A somewhat similar transformation, which is catalyzed by peroxides, has been reported by Staudinger and Ritzenthaler.[6] They found that ethylene and propene combine with sulphur dioxide to form high molecular weight compounds. In the case of ethylene, only ether peroxides served as catalysts, whereas in the other instances, various other higher oxides (for example, ozone and benzoic peroxide) were effective accelerators. The product from propene was believed to be very highly polymeric (molecular weight of 390,000 in one case) because of viscosity measurements of its solution in sulphuric and nitric acid. For ethylene, the structure might be represented either as sulphones:

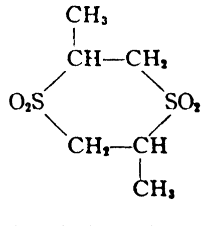
$$\ldots\ldots CH_2{-}CH_2SO_2{-}CH_2{-}CH_2{-}SO_2\ldots\ldots$$

or as sulphinic esters:

$$\ldots\ldots CH_2{-}CH_2{-}O{-}SO{-}CH_2{-}CH_2{-}O{-}SO\ldots\ldots$$

However, the stability of the substance toward oxidation and bromination supports the former structure. Treatment with barium hydroxide resulted in mixtures of barium sulphinates and (from polyethylene- and propene-sulphone, respectively), the compounds:





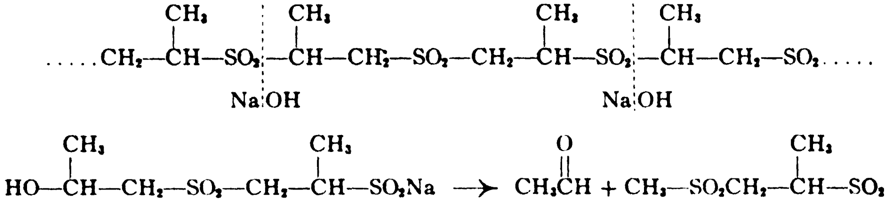
These results have been substantiated by other independent investigations. Hunt and Marvel[7] obtained a much lower value for the molecular weight of polypropenesulphone (about 2000), but later work by Ryden and Marvel[8] using trichloroacetyl derivatives and anilides and analyzing for chlorine gave a molecular weight between 100,000 and 200,000. The researches of Hunt and Marvel largely confirmed the structure proposed by Staudinger and Ritzenthaler. The former work-

[6] H. Staudinger and B. Ritzenthaler, *Ber.*, 1935, 68, 455; *Chem. Abs.*, 1935, 29, 3976; *Brit. Chem. Abs.* A, 1935, 604. See also, Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[7] M. Hunt and C. S. Marvel, *J.A.C.S.*, 1935, 57, 1691; *Chem. Abs.*, 1935, 29, 7276; *Brit. Chem. Abs.* A, 1935, 1349.

[8] L. L. Ryden and C. S. Marvel, *J.A.C.S.*, 1935, 57, 2311; *Brit. Chem. Abs.* A, 1936, 186; *Chem. Abs.*, 1936, 30, 75.

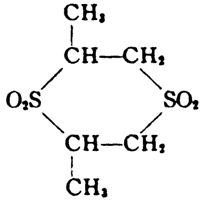
ers tried cleaving the polypropene sulphone by boiling with 10 per cent sodium hydroxide, and obtained two products. The first was a red resinous substance which was identified as the resin formed by boiling acetaldehyde with alkali. This indicated that 2 out of every 6 atoms of carbon in the polysulphone were converted to acetaldehyde on hydrolysis. The second product was shown by synthesis to be the sodium salt of 2-methyl sulphonyl-1-methylethane-1-sulphonic acid. The formation of these products was explained by the equation:



$$\ldots\ldots CH_2-\overset{CH_3}{\overset{|}{C}}H-SO_2\underset{Na\vdots OH}{\vdots}-\overset{CH_3}{\overset{|}{C}}H-CH_2-SO_2-CH_2-\overset{CH_3}{\overset{|}{C}}H-SO_2\underset{Na\vdots OH}{\vdots}-\overset{CH_3}{\overset{|}{C}}H-CH_2-SO_2\ldots\ldots$$

$$HO-\overset{CH_3}{\overset{|}{C}}H-CH_2-SO_2-CH_2-\overset{CH_3}{\overset{|}{C}}H-SO_3Na \longrightarrow CH_3\overset{O}{\overset{\|}{C}}H + CH_3-SO_2CH_2-\overset{CH_3}{\overset{|}{C}}H-SO_3Na$$

The structure assigned by Hunt and Marvel to the product of mild hydrolysis of the polysulphone was somewhat different from the arrangement proposed earlier[8a] in that both methyl groups were on the carbon atoms attached to the same sulphone group.



The combination of sulphur dioxide with methylpropene, pentene-1, and -2, nonene-1, 3-cyclohexylpropene and 3-methylcyclohexene results in the formation of polysulphones, according to Ryden and Marvel.[9] However, many other olefinic compounds, both hydrocarbons and more complex substances, failed to react under the experimental conditions.[10]

Fitch[11] has proposed to make a resinous material by treating a mixture of olefins, (from which unsymmetrical, di-substituted ethylenes have been removed) with sulphur dioxide in the presence of diluents.

Vinyl sulphones and sodium, potassium or calcium bisulphites react in aqueous or alcoholic solution at 100°C. to give β-sulphoethylsulphones:[12] $R-SO_2-CH_2CH_2-SO_3H$. *p*-Tolyl and 2-naphthyl-β-sulphoethylsulphone and *m*-phenylene di(β-sulphoethyl)disulphone have been prepared in this manner.

REACTIONS OF SULPHUR CHLORIDES WITH OLEFINS

Under different conditions, the products of the reaction between sulphur chlorides and unsaturated hydrocarbons may vary considerably in properties. For example, by treating ethylene with sulphur chloride at 50 to 60°C., and then heating the product with sodium polysulphide (Na_2S_5), it is possible to prepare a resistant resin-like material.[13] As is well known,[13a] mixing ethylene with sulphur monochloride at temperatures up to about 70°C. results in the formation of 2,2′-dichlorodiethyl sulphide, or mustard gas (yperite), which first served in chemical warfare during the World War. In connection with this use, mention may be made of the methods employed in detecting this substance in the air.[14] A reaction between mustard gas and bleaching powder, which was described by Stampe and Schröter,[15] leads to the formation of white crystals of unestablished identity. The air to be tested, and air which has been passed over or through bleaching powder, are led into a container. If dichlorodiethyl sulphide is present, white crystals are deposited on the walls of the reaction vessel. Another method which has been suggested[16] consists of passing the gas through a solution containing either 0.1 per cent auric chloride or 0.05 per cent palladous chloride. Mustard gas, if present, causes a yellow colloidal turbidity, and when there in high concentrations, gives reddish-yellow oily droplets. This test is said not to be affected by other chemical warfare agents.

[8a] H. Staudinger and B. Ritzenthaler, *loc. cit.*

[9] L. L. Ryden and C. S. Marvel, *loc. cit.* O. G. Pipik, (*Azer. Neft. Khoz.*, 1935, (4), 61; *Foreign Petroleum Tech.*, 1935, 3, 375, 417; *Chem. Abs.*, 1936, 30, 2375) has also studied the reaction of sulphur dioxide on pentenes.

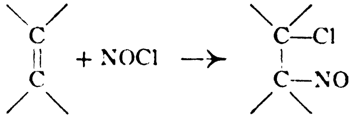
[10] The reactions of diolefins with sulphur dioxide will be discussed in Chapter 27.

[11] L. H. Fitch, Jr., U. S. P. 2,045,592, June 30, 1936, to Phillips Petroleum Co.; *Chem. Abs.*, 1936, 30, 5683.

[12] British P. 450,559, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, 31, 114; *Brit. Chem. Abs.* B, 1936, 972. See also British P. 446,992 and 450,760, 1936; *Chem. Abs.*, 1936, 30, 6851; 1937, 31, 114; *Brit. Chem. Abs.* B, 1936, 972. French P. 797,606, 1936; *Chem. Abs.*, 1936, 30, 8244.

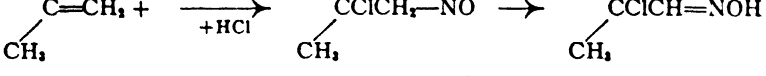
REACTIONS BETWEEN INORGANIC NITROGEN DERIVATIVES AND OLEFINS

The addition of nitrosyl chloride to unsaturates is somewhat analogous to the reactions occurring with other acid chlorides, as mentioned in Chapter 24. The resultants in this case are nitrosochlorides, formed according to the scheme:



The transformation may be effected by treating a solution of the olefinic substance with ethyl nitrite and hydrogen chloride in an anhydrous medium at low temperatures (0°C.). In this way, Cohen and Cook[17] succeeded in synthesizing 2(2′-phenyl)-ethyl-cyclohex-2-en-1-one from 1-(2′-phenyl)-ethylcyclohexene-1 with the intermediate formation of the nitrosochloride, and ketone oxime. The formation of the oxime was effected by boiling the nitrosochloride in pyridine.

Draw and Head[18] have employed a similar reaction in the production of isobutene diamine (1,2-diamino-2-methylpropane) from isobutene. The oxime form of the nitrosochloride was obtained as a white solid (m.p., 104°C.):



The chlorine was replaced by treatment with alcoholic ammonia, and the oxime reduced to an amino group with sodium amalgam and alcohol in acid solution.

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[13] D. F. Twiss and A. E. T. Neale, British P. 430,773, 1935, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1935, **29**, 8407; *J. Inst. Pet. Tech.*, 1935, **21**, 344A; *Brit. Chem. Abs.* B, 1935, 775. See Chapter 20 of this text. Also, Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[13a] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934, 576.

[14] See G. A. Schröter, *Angew. Chem.*, 1936, **49**, 164; *Chem. Abs.*, 1936, **30**, 3116. See also German P. 625,094, 1936, to Drägerwerk Heinrich und Bernhard Dräger; *Chem. Abs.*, 1936, **30**, 2884.

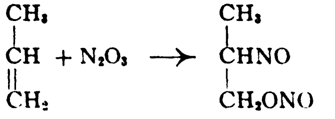
[15] G. Stampe and G. A. Schröter, *Draeger-Hefte*, 1934 (173), 2612; *Chem. Abs.*, 1935, **29**, 449.

[16] M. Obermiller, *Angew. Chem.*, 1936, **49**, 162; *Chem. Abs.*, 1936, **30**, 3115; *Brit. Chem. Abs.* A, 1936, 453.

[17] A. Cohen and J. W. Cook, *J.C.S.*, 1935, 1570; *Chem. Abs.*, 1936, **30**, 1033; *Brit. Chem. Abs.* A, 1936, 75.

[18] H. D. K. Draw and F. S. H. Head, *J.C.S.*, 1934, 49; *Chem. Abs.*, 1934, **28**, 1987; *Brit. Chem. Abs.* A, 1934, 283.

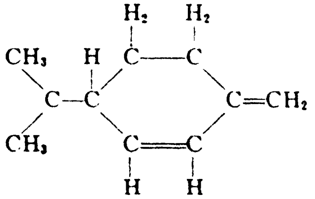
The reactions which take place between olefins and the oxides of nitrogen produce several different types of compounds. The introduction of nitrogen trioxide (the anhydride of nitrous acid) leads to the formation of a nitrosite. Thus Dem'yanov[19] has prepared propene nitrosite by the simultaneous passage of propene and nitrogen trioxide into ether:



$$\begin{array}{l} CH_3 \\ | \\ CH \\ \| \\ CH_2 \end{array} + N_2O_3 \longrightarrow \begin{array}{l} CH_3 \\ | \\ CHNO \\ | \\ CH_2ONO \end{array}$$

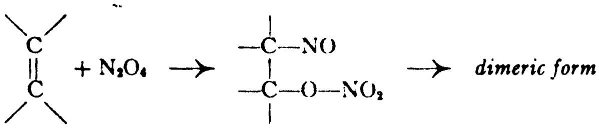
propene nitrosite

The nitrosites are usually bluish liquids which polymerize to give colorless bisnitrosites. By analogous procedures, the nitrosites of butene-1,[20] 2-methylpropene[21] and 2-methylbutene-2[22] have been prepared. If an excess of oxide is used there is said to be danger of the formation of a nitrosate. Gaponenkov[23] synthesized the nitrosites of certain of the terpenes, such as β-phellandrene, by the action of acetic acid on sodium nitrite in the presence of a solution of the hydrocarbon in a light petroleum ether and ethyl ether solvent.[24]



β-phellandrene

Nitrosates may be prepared by the action of nitrogen tetroxide or peroxide on an olefin. The product obtained is the dimeric bisnitrosate, and its formation may be represented by the equation:



$$\begin{array}{c} \diagdown\ \diagup \\ C \\ \| \\ C \\ \diagup\ \diagdown \end{array} + N_2O_4 \longrightarrow \begin{array}{l} -C-NO \\ \quad | \\ -C-O-NO_2 \end{array} \longrightarrow \text{dimeric form}$$

nitrosate

Nitrosates are said to be formed by other reactions. Semenov,[25] for example, obtained a compound of the composition $C_2H_4 \cdot N_2O_4$ from ethylene and nitrogen tetroxide. However, Dem'yanov reported a substance with different physical properties and the formula $C_2H_4 \cdot N_2O_3$.[26] Pentene combines with nitrogen tetroxide to give a nitrosate which decomposes on heating to 100°C.[27] A similar product is prepared from trimethylethylene[28] either by nitrogen tetroxide or by concentrated nitric acid and amyl nitrite in glacial acetic acid solution.

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[19] N. Y. Dem'yanov, *J. Russ. Phys.-Chem. Soc.*, 1901, **33**, 275; *Chem. Zentr.*, 1901, **2**, 333; *J.C.S.*, 1901, **80** (1), 493.

[20] N. Y. Dem'yanov, *Ber.*, 1907, **40**, 245; *J.C.S.*, 1907, **93** (1), 174; *Chem. Zentr.*, 1907, **1**, 628.

[21] K. Sidorenko, *J. Russ. Phys.-Chem. Soc.*, 1906, **38**, 955; *Chem. Zentr.*, 1907, **1**, 399; *J.C.S.*, 1907, **92** (1), 270.

[22] J. Schmidt, *Ber.*, 1902, **35**, 2323, 2336, 3737; *J.C.S.*, 1902, **82** (1), 581, 582; 1903, **84** (1), 3; *Chem. Zentr.*, 1902, **2**, 431, 433. See also A. Hautzsch. *Ber.*, 1902, **35**, 2914, 4120; *J.C.S.*, 1902, **82** (1), 734; 1903, **84** (1), 61; *Chem. Zentr.*, 1902, **2**, 1105; 1903, **1**, 278.

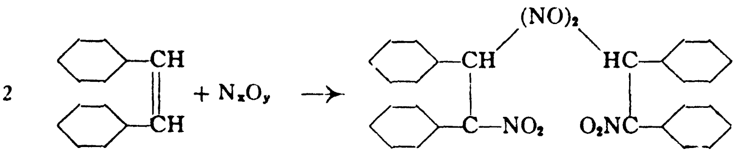
[23] T. K. Gaponenkov. *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 1485; *Brit. Chem. Abs.* **A**, 1936, 729; *Chem. Abs.*, 1936, **30**, 3587.

[24] See also R. Dulou, *Bull. inst. pin.*, 1934, 129; *Chem. Abs.*, 1934, **28**, 7255; *Brit. Chem. Abs.* **A**, 1934, 1106.

[25] Semenov, *Jahresber.*, 1864, 480.

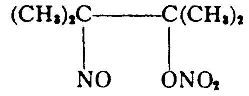
[26] N. Y. Dem'yanov, *Ann. Inst Agron. Moscow*, **4** (4), 155; *Chem. Zentr.*, 1899, **1**, 1064; *J.C.S.*, 1899, **76** (1), 845.

Passage of the nitrogen oxides generated by arsenious oxide and nitric acid into an ethereal solution of stilbene resulted in the formation of the pseudonitrosite[29] (bisnitrosonitro compound):



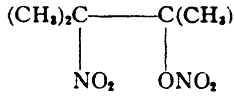
stilbene pseudonitrosite (m.p., 132°C.)

According to Dem'yanov[30] the interaction of tetramethylethylene and nitrogen tetroxide gives rise to a nitrosate and a nitro-nitrate:



$$\underset{\displaystyle NO}{(CH_3)_2\overset{}{C}}\text{———}\underset{\displaystyle ONO_2}{C(CH_3)_2}$$

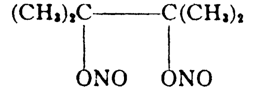
nitrosate



$$\underset{\displaystyle NO_2}{(CH_3)_2C}\text{———}\underset{\displaystyle ONO_2}{C(CH_3)_2}$$

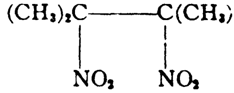
nitro-nitrate

On the other hand, Schmidt[31] reported that the products formed by this reaction were a dinitrite and a dinitrotetramethylethane:



$$\underset{\displaystyle ONO}{(CH_3)_2C}\text{———}\underset{\displaystyle ONO}{C(CH_3)_2}$$

tetramethylethylene glycol dinitrate

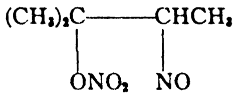


$$\underset{\displaystyle NO_2}{(CH_3)_2C}\text{———}\underset{\displaystyle NO_2}{C(CH_3)_2}$$

dinitrotetramethyl ethane

He reported the formation of diphenyl dinitroethane from stilbene.[32]

There is also some controversy as to the products obtained from the action of nitrogen pentoxide on unsaturates. Thus, Dem'yanov[33] observed the formation of $(C_4H_8N_2O_3)_2$ from butene-2, and of glycol dinitrate (b.p. 114-116°C.) from ethylene. The latter result has been found to occur when the ethylene has not been rigorously dried.[34] Dem'yanov found furthermore that, whereas trimethylethylene reacted with nitrogen pentoxide to give a nitrosite, tetramethylethylene formed a



$$\underset{\displaystyle ONO_2}{(CH_3)_2C}\text{———}\underset{\displaystyle NO}{CHCH_3}$$

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[27] See O. Wallach, *Ann.*, 1887, **241**, 288; *J.C.S.*, 1888, **54**, 37. Guthrie, *Ann.*, 1860, **116**, 248; 1861. **119**, 84. J. Schmidt, *Ber.*, 1903, **36**, 1765; *Chem. Zentr.*, 1903, **2**, 100. A Schaarschmidt and H. Hofmeier, *Ber.*, 1925, **58**, 1047; *Chem. Abs.*, 1925, **19**, 2634; *J.C.S.*, 1925, **128** (1), 877.

[28] F. W. Klingstedt, *Ber.*, 1925, **58**, 2363; *Brit. Chem. Abs.* **A**, 1926, **44**; *Chem. Abs.*, 1926, **20**, 1049. See also J. Schmidt, *Ber.*, 1902, **35**, 2336; *J.C.S.*, 1902, **82** (1), 582; *Chem. Zentr.*, 1902, **2**, 433.

[29] H. Wieland and E. Blümich, *Ann.*, 1921, **424**, 75; *Chem. Abs.*, 1921, **15**, 2857; *J.C.S.*, 1921, **120** (1), 552. See also P. Karrer, "Lehrbuch der Organischen Chemie," Georg Thieme, Leipzig, **1933**, 58. L. Monto and F. Bucci, *Gazz. chim. ital.*, 1933, **63**, 708; *Chem. Zentr.*, 1934, **1**, 1483; *Chem. Abs.*, 1934, **28**, 2686.

[30] N. Y. Dem'yanov, *loc. cit.*

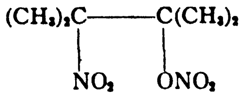
[31] J. Schmidt, *Ber.*, 1903, **36**, 1775; *J.C.S.*, 1903, **84** (1), 597; *Chem. Zentr.*, 1903, **2**, 102.

[32] J. Schmidt, *Ber.*, 1901, **34**, 619, 623, 3536; *J.C.S.*, 1901, **80** (1), 266; 1902, **82** (1), 21; *Chem. Zentr.*, 1901, **1**, 834; 1901, **2**, 1309. See also H. Wieland and E. Blümich, *Ann.*, 1921, **424**, 100; *Chem. Abs.*, 1921, **15**, 2858; *J.C.S.*, 1921, [illegible] (1), 554.

[33] N. Y. Dem'yanov, *loc. cit.*

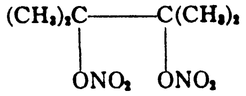
[34] L. B. Haines and H. Adkins, *J.A.C.S.*, 1925, **47**, 1419; *Chem. Abs.*, 1925, **19**, 1855; *J.C.S.*, 1925, **128** (1), 801.

mixture of the nitro-nitrate and dinitrate:



$(CH_3)_2C(NO_2)-C(CH_3)_2(ONO_2)$

nitro-nitrate



$(CH_3)_2C(ONO_2)-C(CH_3)_2(ONO_2)$

dinitrate

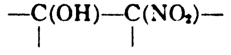
The action of nitric acid, fuming nitric acid and nitrating acid (nitric and sulphuric acids) on ethylene gives different results. Kekule[35] stated that cold, mixed sulphuric-nitric acid produced ethylene glycol nitrate nitrite ($ONOCH_2CH_2$-ONO_2). On the other hand, Akestorides[36] held that ethylene was oxidized by fuming nitric acid to give oxalic acid and carbon monoxide. Haitinger[37] reported that the direct nitration of 2-methylpropene gave small amounts of the 2-methyl-1-nitropropene-1 and some butene dinitrite:[38] $(CH_3)_2C(ONO)-CH_2(ONO)$. There was, however, considerable oxidation leading to the formation of carbon dioxide, aliphatic acids and acetone.

Woodbury[39] has found that the direct nitration of an olefin with 2 to 4 carbon atoms by mixed nitric and sulphuric acid gives a highly explosive material. The nitrated substance is said to consist of a mixture of ethylene glycol dinitrate and 2-nitroethyl nitrate. A typical example of an explosive mixture is:

2-Nitroethyl nitrate	6 per cent
Ethylene glycol dinitrate	12 ” ”
Trinitroglycerol	22 ” ”
Sodium nitrate	46 ” ”
Wood meal	13 ” ”
Chalk	1 ” ”

The advantages of the incorporation of this nitrated ethylene are said to be lower cost (since cracking gases are employed as raw material) and lowering of the freezing point of dynamite prepared from it.[40]

The mechanism of the reaction of nitric acid and an olefin has been studied by Michael and Carlson[41] and by Wieland and co-workers.[42] The latter believed that combination took place by introduction of HO and NO_2 groups to form a nitrohydrine:



$-C(OH)-C(NO_2)-$

The hydroxyl group was then esterified to form α-nitroethyl-nitrate. On the other hand, according to Michael and Carlson, nitration of ethylenic compounds is not caused by nitric acid, but by oxides of nitrogen present in the reaction mixture. They state, moreover, that nitration by mixed nitric and sulphuric acids probably occurs by the addition:

---

[35] A. Kekulé, *Ber.*, 1869, 2, 329. *Cf.* L. Haitinger, *Monatsh.*, 1881, 2, 286; *J.C.S.*, 1881, 40, 1114; *Chem. Zentr.*, 1881, 403.

[36] F. Akestorides, *J. prakt. Chem.*, 1877, 15 (2), 62; *J.C.S.*, 1877, 32, 287; *Chem. Zentr.*, 1877, 146.

[37] L. Haitinger, *loc. cit.*

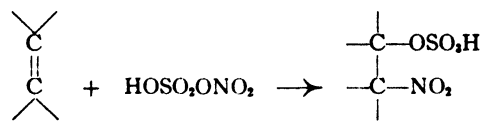
[38] Ethylene and propene dinitrites (b.p. 96-98°C. and 108-110°C., respectively) have been described by G. Bertoni, *Gazz. chim. ital.*, 1885, 15, 361; *J.C.S.*, 1886, 50, 217. *Ann. Chim. Farm.*, 1886, 1, 273; *Chem. Zentr.*, 1887, 35; *J.C.S.*, 1887, 52, 458.

[39] C. A. Woodbury, U. S. P. 1,485,003, Feb. 26, 1924, to E. I. du Pont de Nemours & Co.; *J.S.C.I.*, 1924, 43, 4953; *Chem. Abs.*, 1924, 18, 1391.

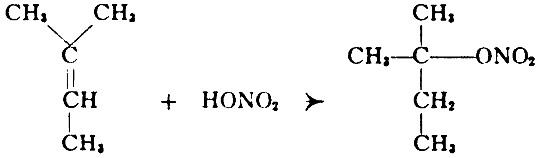
[40] See also the application of glycol dinitrate for this purpose. Chapter 22.

[41] A. Michael and G. H. Carlson, *J.A.C.S.*, 1935, 57, 1268; *Brit. Chem. Abs.* A, 1935, 1103; *Chem. Abs.*, 1935, 29, 5811. Also N. Y. Dem'yanov and V. V. Williams, *Bull. acad. sci. U.R.S.S.*, 1931, 1123; *Chem. Abs.*, 1932, 26, 3238.

[42] H. Wieland and E. Sakellarios, *Ber.*, 1920, 53, 201; *J.C.S.*, 1920, 118 (1), 280; *Chem. Abs.*, 1920, 14, 2636. H. Wieland and F. Rahn, *Ber.*, 1921, 54, 1770; *J.C.S.*, 1921, 120 (1), 782; *Chem. Abs.*, 1922, 16, 903.



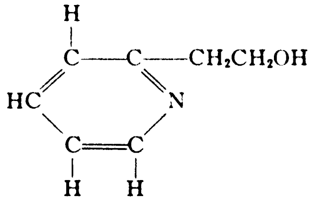
with the subsequent replacement of the $-SO_3H$ group by the more active nitro group. In contrast to the results of Wieland and Rahn,[43] Michael and Carlson show that at −20°C. the addition of trimethylethylene to an excess of "absolute nitric acid" in carbon tetrachloride gave largely the ester formed by the reaction.



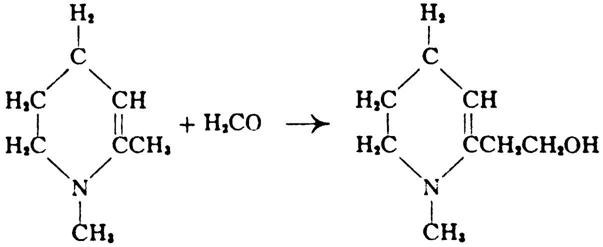
On standing at room temperature for 3 or 4 days, the *ter*-amyl nitrate produced in the above manner decomposed into high boiling substances. Dimethylaniline gave rise to isoamylene and the amine nitrate. Saponification of the latter by warm aqueous alkali produced isoamylene and 2-methylbutanol-2.

Reaction of Olefins with Aldehydes

These condensations were first investigated in 1889 by Ladenburg,[44] who reported the combination of 2-methylpyridine and formaldehyde which resulted in the formation of a compound which he called "α-picolyalkine," i.e., 2-(2′-pyridyl)-ethanol.



An analogous procedure using acetaldehyde gave the corresponding derivative of isopropanol. Subsequently, Lipp[45] found that an aqueous solution of methyltetrahydropicoline and formalin condensed to yield a base, according to the reaction:



Ladenburg,[46] however, stated that the product could be hydrogenated and dehydrated to give a bicyclic compound, and he assigned a somewhat different formula:

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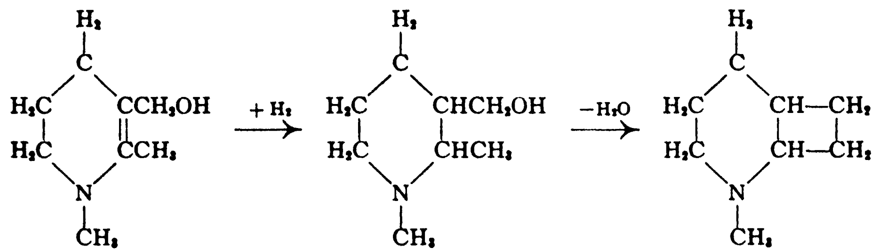
[43] H. Wieland and F. Rahn, *loc. cit.*

[44] A. Ladenburg, *Ber.*, 1889, **22**, 2583; *Chem. Zentr.*, 1889, **2**, 987; *J.C.S.*, 1890, **58**, 67. *Cf. Ber.*, 1891, **24**, 1619; *Chem. Zentr.*, 1891, **2**, 174; *J.C.S.*, 1891, **60**, 1093.

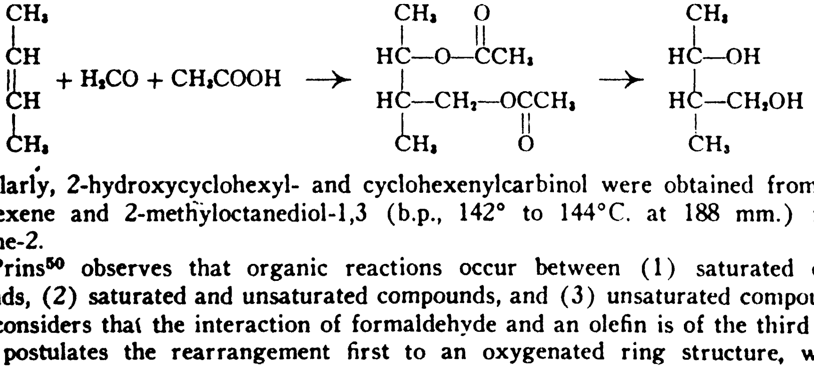
[45] A. Lipp, *Ann.*, 1896, **294**, 135; *Chem. Zentr.*, 1897, **1**, 386; *J.C.S.*, 1897, **72** (1), 229.

[46] A. Ladenburg, *Ber.*, 1898, **31**, 286; *Chem. Zentr.*, 1898, **1**, 743; *J.C.S.*, 1898, **74** (1), 338; *Ann.*, 1897, **295**, 370; *Chem. Zentr.*, 1897, **1**, 1057; *J.C.S.*, 1897, **72** (1), 432.



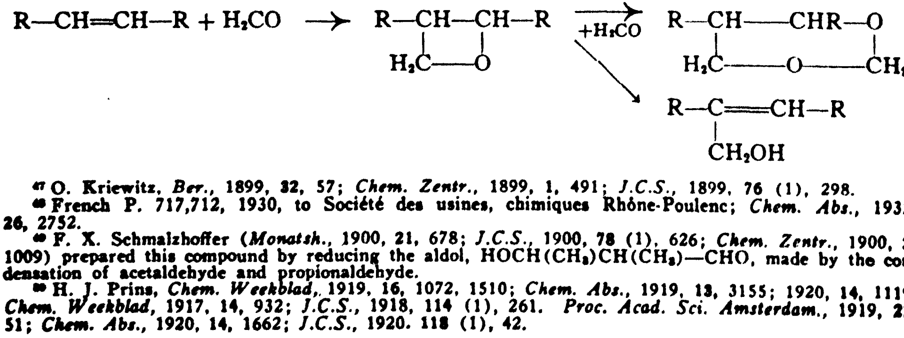
Union between formaldehyde and terpenes such as pinene, limonene and dipentene, may be effected by heating under pressure for about 12 hours at temperatures of 170° to 195°C.[47] Alcohol is employed as the solvent. The addition of formaldehyde apparently results in the formation of primary alcohols, as the reaction products readily give characteristic esters with either acetic anhydride or benzoyl chloride.

Aliphatic or hydroaromatic olefins are said to condense with formaldehyde to form glycols.[48] Thus, 45 liters of butene-2 may be absorbed in a solution containing 66 g. trioxymethylene in 440 g. glacial acetic acid and 62 g. concentrated sulphuric acid. The temperature must be maintained below 40°C. The solution is diluted with 500 cc. water and the diacetate of 1,2-dimethylpropanediol-1,3 separates as a liquid. Rectification gives 300 g. of product (b.p., 100-108°C. at 188 mm.) from which the glycol[49] (b.p., 112-118°C. at 25 mm.) may be prepared by saponification.



Similarly, 2-hydroxycyclohexyl- and cyclohexenylcarbinol were obtained from cyclohexene and 2-methyloctanediol-1,3 (b.p., 142° to 144°C. at 188 mm.) from octene-2.

Prins[50] observes that organic reactions occur between (1) saturated compounds, (2) saturated and unsaturated compounds, and (3) unsaturated compounds. He considers that the interaction of formaldehyde and an olefin is of the third type and postulates the rearrangement first to an oxygenated ring structure, which reacts further to give three possible products:



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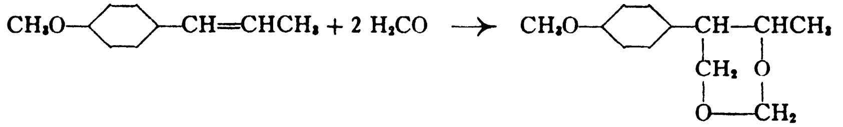
[47] O. Kriewitz, *Ber.*, 1899, 32, 57; *Chem. Zentr.*, 1899, 1, 491; *J.C.S.*, 1899, 76 (1), 298.

[48] French P. 717,712, 1930, to Société des usines chimiques Rhône-Poulenc; *Chem. Abs.*, 1932, 26, 2752.

[49] F. X. Schmalzhoffer (*Monatsh.*, 1900, 21, 678; *J.C.S.*, 1900, 78 (1), 626; *Chem. Zentr.*, 1900, 2, 1009) prepared this compound by reducing the aldol, $HOCH(CH_3)CH(CH_3)—CHO$, made by the condensation of acetaldehyde and propionaldehyde.

[50] H. J. Prins, *Chem. Weekblad*, 1919, 16, 1072, 1510; *Chem. Abs.*, 1919, 13, 3155; 1920, 14, 1119. *Chem. Weekblad*, 1917, 14, 932; *J.C.S.*, 1918, 114 (1), 261. *Proc. Acad. Sci. Amsterdam.*, 1919, 22, 51; *Chem. Abs.*, 1920, 14, 1662; *J.C.S.*, 1920. 118 (1), 42.

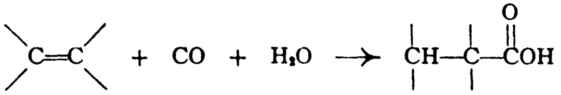
The presence of acetic acid may cause the formation of an acetate. Thus, 104 g. of styrene are added to a solution of 33 g. trioxymethylene and 32 g. concentrated sulphuric acid in 320 g. glacial acetic acid, the temperature being kept below 50°C. After several hours, the mixture is diluted with water and extracted. The oil recovered in this way is distilled and saponified. The product consists of 2-phenylpropanediol-1,3 and its methylene ether. However, from *p*-propenylmethoxybenzene (anethole) only the methylene ether was obtained.



There has been some projected commercial application of the reactions of aldehydes and olefins in forming resins and in refining petroleum fractions. Day[51] treated furfuraldehyde and a cracked gasoline with concentrated sulphuric acid. The mixture was refluxed and on cooling, a black gelatinous mass separated after about 20 minutes. By mixing the mass with wood flour, it can be worked into molded products. Thus from the olefins obtained in the sulphur dioxide extraction of cracked gasoline, acetone-soluble resins may be synthesized which are reported utilizable as substitutes for shellac. Levine[52] has proposed refining cracked distillates by vapor phase reaction with formaldehyde or acetaldehyde in the presence of hydrogen chloride and aluminum or zinc. On the other hand, Fulton[53] has recommended the removal of undesirable constituents in the presence of acetic acid and a condensing agent. Oil-soluble resinous substances may be separated by distillation. An oil may be treated, for example, with a mixture of equal parts by weight of concentrated sulphuric acid, glacial acetic acid and formaldehyde, and then distilled.

REACTIONS OF OLEFINS AND CARBON MONOXIDE

The commercial applications of carbon monoxide are so numerous that it is impossible to treat them except cursorily in this volume. The carbon monoxide-hydrogen synthesis of hydrocarbons will be discussed in Chapter 52. At this point a short discussion will be given of the synthesis of acids by the interaction of carbon monoxide, olefins and steam:



A large number of catalysts have been suggested to promote this reaction. Thus, Carpenter[54] has proposed several promoters such as non-volatile inorganic acids (e.g., phosphoric) either alone or with a volatile halide such as hydrogen chloride, or the halides of alkali or alkaline earth metals or of copper, iron, cobalt, nickel, bismuth, manganese, lead, titanium, zinc or cadmium alone, or with hydrogen halides, and further, the combined acidic oxides of groups 3 to 6 of the periodic system (such as silicomolybdic acid). The acid salts of phosphorus, arsenic, tungsten, molybdenum, uranium, chromium, vanadium, boron, silicon, or zirconium, (for instance, calcium monophosphate) were also suggested. Woodhouse[55] prefers to form the volatile inorganic acid (such as hydrochloric) *in situ* from chlorine in the presence of activated carbon. Among other catalysts recommended are: boron phosphate,[56] ammonium halides,[57] and alkali or alkaline earth fatty acid salts, alkoxides, carbonates or hydroxides.[58]

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[51] R. B. Day, U. S. P. 1,933,715, and 1,933,716, Nov. 7, 1933, to Universal Oil Products Co.: *Brit. Chem. Abs.* B, 1934, 805; *Chem. Abs.*, 1934, **28**, 664. See also G. S. Petrov, Russian P. 32,725. 1933; *Chem. Abs.*, 1934. **28**, 3581.

[52] I. Levine, U. S. P. 1,974,311, Sept. 18, 1934, to Universal Oil Products Co.; *Chem. Abs.*, 1934, **28**, 6993; *J. Inst. Pet. Tech.*, 1934, 20, 582A.

[53] S. C. Fulton, U. S. P. 2,018,715, Oct. 29, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 279. U. S. P. 2,035,123, March 24, 1936; *Chem. Abs.*, 1936, **30**, 3220.

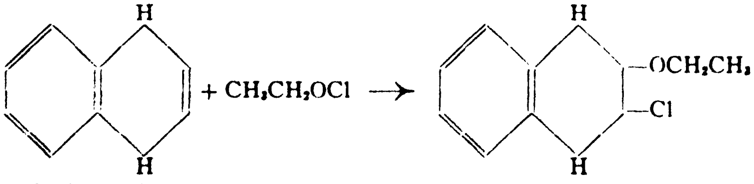
[54] G. B. Carpenter, U. S. P. 1,924,763, 1,924,766, 1,924,767, 1,924,768 and 1,924,769, Aug. 29, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1934, 534; *Chem. Abs.*, 1933, **27**, 5340. U. S. P. 1,957,939, May 8, 1934; *Chem. Abs.*, 1934, **28**, 4071; *Brit. Chem. Abs.* B, 1935, 262. U. S. P. 1,981,081, Nov. 20, 1934; *Brit. Chem. Abs.* B, 1935, 939. U. S. P. 2,008,348; July 16 1935; *Brit. Chem. Abs.* B, 1936, 633; *Chem. Abs.*, 1935, **29**, 5863. U. S. P. 2,015,065, Sept. 24, 1935, *Brit. Chem. Abs.* B, 1936, 1081; *Chem. Abs.*, 1935, **29**, 7345. Canadian P. 339,933, 339,935, 339,937, 1934; *Chem. Abs.*, 1934, **28**, 3082.

A process involving the liquid phase condensation of carbon monoxide and the unsaturated substances obtained in the cracking of petroleum oils has been advocated by Schalch.[59] In this method, the reactions are carried out with finely divided nickel, or various metallic oxides, suspended in the liquid.

Hardy[60] reported the interaction of ethylene, propene and butene-2 with carbon monoxide and steam in the presence of phosphoric acid with the formation of propionic, isobutyric and trimethylacetic (i.e., pivalic) acids. This confirmed his belief that the reaction of alcohols, carbon monoxide and steam proceeded by the intermediate elimination of water.[61]

CONDENSATION OF ALKENES WITH ALKYL HYPOCHLORITES

The addition of alkoxy chlorides (alkyl hypochlorites) to double bonds is not generally understood, and there is some difference of opinion as to the products formed. Both methyl and ethyl hypochlorite have been prepared by Sandmeyer through treatment of an alkaline solution of the alcohol with chlorine.[62] No reaction was observed when carbon dioxide, ethylene, amylene, acetylene or diethyl fumarate was allowed to act on ethyl hypochlorite. Subsequently, Goldschmidt, Endres and Dirsch[63] investigated the reaction of the latter substance. They reported that in most cases saturation of double bonds occurred as though hypochlorous acid were present. Thus amylene, cyclohexene and indene gave the corresponding chlorohydrins. Similar results were brought about by the reaction with acetylenes: phenylacetylene, for example, giving ω,ω-dichloroacetophenone. In other instances, ethyl hypochlorite acted as chlorinating agent, but it apparently added to 1,4-dihydronaphthalene with the formation of an inseparable mixture which included the product of the addition of an ethoxy and chloro group



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[55] J. C. Woodhouse, U. S. P. 1,924,762, Aug. 29, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, **27**, 5339; *Brit. Chem. Abs.* **B**, 1935, 534.

[56] W. E. Vail, U. S. P. 1,924,764, Aug. 29, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, **27**, 5340; *Brit. Chem. Abs.* **B**, 1934, 534.

[57] A. T. Larson and W. E. Vail, U. S. P. 1,924,765, Aug. 29, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, **27**, 5340; *Brit. Chem. Abs.* **B**, 1934, 534.

[58] W. E. Vail, U. S. P. 2,000,053, May 7, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1936, 488; *Chem. Abs.*, 1935, **29**, 4023.

[59] J. Schalch, U. S. P. 1,973,662, Sept. 11, 1934, to Van Schaack Bros. Chemical Works; *Chem. Abs.*, 1934, **28**, 6723; *Brit. Chem. Abs.* **B**, 1935, 761.

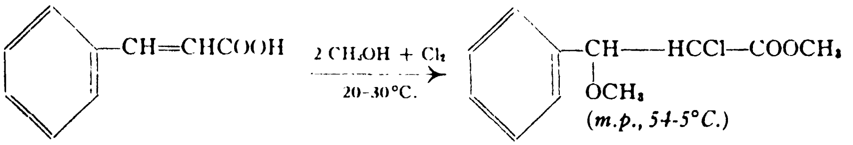
[60] D. V. N. Hardy, *J.C.S.*, **1936**, 364; *Brit. Chem. Abs.* **A**, 1936, 590; *Chem. Abs.*, 1936, **30**, 3771.

[61] See D. V. N. Hardy, *J.C.S.*, **1936**, 358, 362; *Chem. Abs.*, 1936, **30**, 3776; *Brit. Chem. Abs.* **A**, 1936, 590. W. E. Vail, U. S. P. 1,979,717, Nov. 6, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 893. Canadian P. 342,957, 1934, to Canadian Industries Ltd.; *Chem. Abs.*, 1934, **28**, 6444.

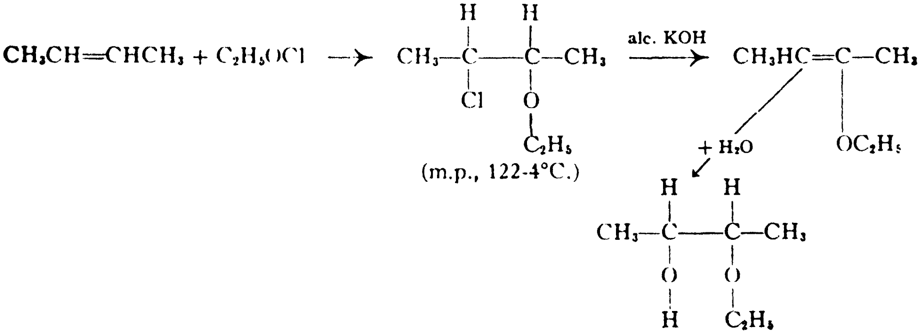
[62] T. Sandmeyer, *Ber.*, 1885, **18**, 1767; *J.C.S.*, 1885, **48**, 1045. *Ber.*, 1886, **19**, 857; *J.C.S.*, 1886, **50**, 607.

[63] S. Goldschmidt, R. Endres and R. Dirsch, *Ber.*, 1925, **58**, 572; *Chem. Abs.*, 1925, **19**, 2031.

The union of hypochlorous esters with olefinic acids yields considerable quantities of the chlorohydrins or their lactones, but only small amounts of the chlorohydrin ethers. Thus, hex-3-enoic acid and ethyl hypochlorite in ether gave 93 per cent of isomeric 2-chlorohexolactone.[64] On the other hand, Jackson and Pasiut[65] have obtained small proportions of 1-chloro-2-alkoxy-2-phenylpropionic acids (substituted dihydrocinnamic acids) by the reaction of cinnamic acid in alcohol and chlorine. The alcohols used were ethyl and *ter*-butyl, the conversion being slightly better with the latter. With methanol, Jackson[66] reported 55 per cent of the methyl ester of 1-chloro-2-methoxy-2-phenyl propionic acid. Likewise, bromine could be substituted for chlorine.



Likhosherstov and Alekseev[67] have studied the action of alkyl hypochlorites on butene-2 (pseudo-butene) and reported the formation of ethers of 3-chlorobutanol-2. The reactant was prepared by the method of Sandmeyer,[68] and reacted with the olefin by dropwise addition to the latter at —15°C. The alcohols corresponding to the hypochlorite were used as solvents. The process, termed chloroalkoxylation, followed the equation:



$$CH_3CH{=}CHCH_3 + C_2H_5OCl \longrightarrow CH_3-\underset{Cl}{\overset{H}{C}}-\underset{\underset{C_2H_5}{O}}{\overset{H}{C}}-CH_3 \xrightarrow{\text{alc. KOH}} CH_3HC{=}\underset{OC_2H_5}{C}-CH_3$$

(m.p., 122-4°C.)

$$\xrightarrow{+H_2O} CH_3-\underset{\underset{H}{O}}{\overset{H}{C}}-\underset{\underset{C_2H_5}{O}}{\overset{H}{C}}-CH_3$$

The subsequent reactions of the chloro-ether to give an ether of enolic butanone-2, and hydration of the latter are also shown. The halogenated ethers are said to be colorless liquids with pleasant odor. They are distillable at atmospheric pressure, and are miscible with alcohol, ether and chloroform, but not with water.[69]

Langedijk[70] has also employed a mixture of *ter*-butyl hypochlorite and water in a gas-tight container as an absorbent for ethylene. From the reaction mixture, *ter*-butyl alcohol and ethylene glycol were recovered, the latter in 75 per cent yield.

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[64] G. F. Bloomfield and E. H. Farmer, *J.C.S.*, **1932**, 2062; *Chem. Abs.*, 1932, **26**, 5065.

[65] E. L. Jackson and L. Pasiut, *J.A.C.S.*, 1927, **49**, 2071; *Chem. Abs.*, 1927, **21**, 3051; *Brit. Chem. Abs.* **A**, 1927, 969.

[66] E. L. Jackson, *J.A.C.S.*, 1926, **48**, 2166; *Chem. Abs.*, 1926, **20**, 299; *Brit. Chem. Abs.* **A**, 1926, 1023.

[67] M. V. Likhosherstov and L. V. Alekseev, *J. Gen. Chem. (U.S.S.R.)*, 1934, **4**, 1279; *Chem. Abs.*, 1935, **29**, 3306. See also, M. V. Likhosherstov, A. A. Petrov and S. V. Alekseev, *J. Chem. Ind.* (*Moscow*), 1935, **12**, 607; *Chem. Abs.*, 1935, **29**, 7946; *Brit. Chem. Abs.* **B**, 1935, 1084.

[68] T. Sandmeyer, *Ber.*, 1885, **18**, 1767; *J.C.S.*, 1885, **48**, 1045. *Ber.*, 1886, **19**, 857; *J.C.S.*, 1886, **50**, 607.

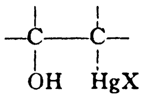
[69] C. G. Harford (U. S. P. 2,054,814, Sept. 22, 1936, to Arthur D. Little, Inc.; *Chem. Abs*, 1936, **30**, 7584) has prepared esters of alkene chlorohydrins by treatment of an olefin such as butene-2 with *ter*-butyl hypochlorite and acetic acid.

[70] S. L. Langedijk, Canadian P. 356,305, 1936, to Shell Development Co.; *Chem. Abs.*, **1936**, **30**, **2989**.

Ethylene glycol hypochlorite has been said to react with ethylene or other olefins to produce a dichlorodialkylether.[71]

COMPOUNDS OF OLEFINS WITH INORGANIC SALTS

Many olefins react with inorganic salts to form well-defined compounds of a complex nature which are usually represented by simple ratios of molecules of the compounds. Mercury salts, for example, appear to have an especial tendency toward this type of combination, and give a compound with the probable formula:



$$-\underset{OH}{\overset{|}{\underset{|}{C}}}-\underset{HgX}{\overset{|}{\underset{|}{C}}}-$$

This reaction is relatively specific for olefins, and has been used in their quantitative estimation.[72] The substances obtained by the action of mercuric acetate on cyclohexene, methylcyclohexene or octahydronaphthalene have also been suggested as disinfectants for grain.[73]

The earliest example of the formation of an olefin complex was reported by Zeise in 1831.[74] He obtained the compound $K(PtCl_3 \cdot C_2H_4) \cdot H_2O$ from the reduction of platinic chloride with alcohol. The analogous derivatives of propene and pentene have been investigated[75] as well as the corresponding potassium ethylenetribromoplatinite $K(PtBr_3 \cdot C_2H_4)$. The compounds of unsaturated acids, alcohols and aldehydes have been prepared by Biilmann and his co-workers[76] and by Pfeiffer and Hoyer.[77] The reactions of Zeise's salt, i.e., potassium ethylene trichloroplatinite monohydrate, have been investigated by Anderson.[78] Ethylene is liberated by the action of potassium cyanide or of pyridine on the salt, whereas with water at 90°C. or higher, the effect is partly the freeing of ethylene and partly the formation of acetaldehyde and platinum:

$$K(PtCl_3 \cdot C_2H_4) + H_2O \longrightarrow KCl + 2\ HCl + Pt + CH_3CHO$$

Although ethylene reacts readily, it was noted that styrene, indene, cyclohexene, 1,1-diphenylethylene and 1-phenyl-1-methylethylene were progressively more difficult to interact to give complexes. Kharasch and Ashford[79] have isolated coordination compounds of the type $(Un \cdot PtX_2)_2$ by combination of a platinic halide $(PtCl_3)$ with an unsaturated compound (indicated above by Un). These investigators point out that although the most direct method for the preparation of these substances would be by direct union of olefins and platinous chloride $(PtCl_2)$, yet because of the insolubility and inertness of the latter, attempts to apply this method are usually unsatisfactory. Their procedure consisted in suspending platininc chloride in glacial acetic acid; adding the olefin and warming on a steam bath to effect solution and reaction.

By passing ethylene into an ethereal solution containing a hydrogen chloride molybdic anhydride complex, glycol molybdate is said to result.[80]

[71] French P. 773,140, 1934, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, 29, 1432.

[72] See Chapter 50 of this text and Chapters 25 and 50 of Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[73] French P. 768,605, 1934, to Deutsche Hydrierwerke A.-G.; *Chem. Abs.*, 1935, 29, 542.

[74] Zeise, *Pogg. Ann.*, 1831, 21, 497.

[75] K. Birnbaum, *Ann.*, 1869, 145, 67.

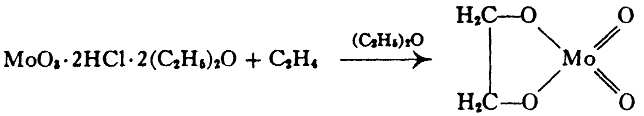
[76] E. Biilmann and A. Hoff, *Rec. trav. chim.*, 1916, 36, 289, 306; *Chem. Zentr.*, 1917, 1, 562; *Chem. Abs.*, 1917, 11, 3035, 3036; *J.C.S.*, 1917, 112 (1), 123.

[77] P. Pfeiffer and H. Hoyer, *Z. anorg. allgem. Chem.*, 1933, 211, 241; *Chem. Abs.*, 1933, 27, 5269; *Brit. Chem. Abs.* A, 1933, 581.

[78] J. S. Anderson, *J.C.S.*, 1934, 971; *Chem. Abs.*, 1934, 28, 6148; *Brit. Chem. Abs.* A, 1934, 994. *J.C.S.*, 1936, 1042; *Chem. Abs.*, 1936, 30, 6699; *Brit. Chem. Abs.* A, 1936, 1098.

[79] M. S. Kharasch and T. A. Ashford. *J.A.C.S.*, 1936, 58, 1733; *Chem. Abs.*, 1936, 30, 8060.

[80] J. Bye, *Compt. rend.*, 1936, 203, 321; *Chem. Abs.*, 1936, 30, 6705.



$$MoO_2 \cdot 2HCl \cdot 2(C_2H_5)_2O + C_2H_4 \xrightarrow{(C_2H_5)_2O}$$

The organometallic product is a white hygroscopic powder, soluble in alcohols, but decomposed by water. It turns blue in the light. In this connection it is interesting to note that a somewhat similar reaction takes place if either cyclohexene or ethylene is treated with mercuric nitrate and iodine.[81] The product is thought to be an iodo alkyl nitrate:

$$2CH_2{=}CH_2 + Hg(NO_3)_2 + 2\ I_2 \xrightarrow[\text{solution}]{(C_2H_5)_2O} HgI_2 + 2\ CH_2ICH_2ONO_2$$

A reaction which is somewhat similar to those between olefins and various organic oxygen compounds occurs when aqueous solutions of alkali hydroxides and basic aluminum compounds are heated with olefins at 300° to 400°C. at superatmospheric pressures.[82] In this manner, propene may be oxidized to give potassium acetate in a 30 per cent yield.

$$C_3H_6 + KOH + H_2O \longrightarrow KOOCCH_3 + CH_4 + H_2$$

Similarly by heating 250 g. of water and 90 g. potassium hydroxide under 25.5 atmospheres pressure of ethylene in a 2 liter autoclave, Hofsäsz has been able to obtain 71.5 g. of acetic acid.[83]

By condensation of olefinic substances with unsaturated carbonyl compounds, such as maleic anhydride, it is said to be possible to prepare substituted polycarboxylic acids.[84] Dreyfus[85] has suggested that olefins such as ethylene may be condensed with cellulose and other carbohydrates by heating at 100° to 200°C. in the presence of a catalyst and under pressure.

OTHER REACTIONS OF OLEFINS

The action of thiocyanogen on olefins is similar in many respects to that of the halogens. This principle has been employed in the analysis of fats and oils analogous to the iodine method.[86] The solution of thiocyanogen may be prepared by suspending pure, dry lead thiocyanate in anhydrous acetic acid and adding bromine, according to Krassilchik.[87] Solutions below 0.1*N* are said to be stable. A disadvantage of this reagent, which has been used in the study of many oils and fats[88] is the time necessary for equilibrium. Caldwell and Piontkowski[89] have found that 1 to 2 hours sufficed for reaction of an oil with the Hanus iodine bromide solution, whereas 47 hours were required with the Kaufmann thiocyanogen reagent. There is also some interference from alcoholic substances and from steric hindrance of the double bond.

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[81] L. Birckenbach and J. Goubeau, *Ber.*, 1934, **67**, 1420; *Chem. Abs.*, 1935, **29**, 125; *Brit. Chem. Abs.* **A**, 1934, 995.

[82] E. C. Britton, H. S. Nutting and M. E. Huscher, U. S. P. 2,000,878, May 7, 1935, to Dow Chemical Co.; *Chem. Abs.*, 1935, **29**, 4026; *Brit. Chem. Abs.* **B**, 1936, 488.

[83] M. Hofsäsz, U. S. P. 1,951,896, Mar. 20, 1934, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 3424.

[84] British P. 395,193, 1932, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1933, 856; *Chem. Abs.*, 1934, **28**, 270. Dutch P. 32,029, 1934; *Chem. Abs.*, 1934, **28**, 3743. French P. 743,302, 1933; *Chem. Abs.*, 1933, **27**, 3720.

[85] H. Dreyfus, French P. 750,493, 1933; *Chem. Abs.*, 1934, **28**, 894.

[86] See Chapter 50.

[87] A. Krassilchik, *Ann. combustibles liquides.*, 1935, **10**, 923; *J. Inst. Pet. Tech.*, 1936, **22**, 44A; *Chem. Abs.*, 1936, **30**, 1023; *Brit. Chem. Abs.* **A**, 1936, 598.

[88] See, for example, N. N. Godbole and Sadgopal, *Allgem. Oel-u. Fett-Ztg.*, 1934, **31**, 435; *Chem. Abs.*, 1935, **29**, 4959; *Brit. Chem. Abs.*, **B**, 1935, 68.

[89] B. P. Caldwell and F. A. Piontkowski, *J.A.C.S.*, 1934, **56**, 2086; *Chem. Abs.*, 1935, **29**, 119; *Brit. Chem. Abs.* **A**, 1934, 1331.

According to Lippmann, benzoyl peroxide and amylene (a mixture of isomeric hydrocarbons boiling at 35° to 40°C.) combine quite violently at 100°C. and 10 atmospheres pressure.[90] The reaction mixture was separated into benzoic acid, small quantities of benzoic anhydride, pentane, carbon dioxide and a light oil, of a pleasant ethereal odor. The latter was evidently a mixture of benzoates, as on saponification it yielded potassium benzoate and a clear yellow oil, of which about one-half consisted of an amyl ether ($C_{10}H_{20}O$, b.p., 198-203°C.).

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[90] E. Lippmann, *Monatsh.*, 1885, **5**, 559; *J.C.S.*, 1885, **48**, 366.

Chapter 26

Polymerization of Monolefins and Diolefins. Synthetic Polymerization Products

Numerous researches on the polymerization of olefins have been stimulated by the huge volumes of gaseous unsaturated hydrocarbons obtained in the cracking industry. Formerly these substances were considered of little value and allowed to escape into the atmosphere, but later developments have led to their recovery and subsequent utilization, particularly conversion to alcohols[1] (both mono- and dihydric) or to hydrocarbons of higher molecular weights by polymerization. The latter is exemplified by the production of synthetic gasoline or lubricating oils and synthetic rubber. Egloff has shown that in 1935 alone there was available a potential supply of 9,000,000,000 gallons of polymer gasoline, which could have been recovered from cracking gas as the source of raw materials.[2]

Strictly speaking, polymerization from this standpoint involves the combination of unsaturated molecules to form larger molecules. Paraffins do not yield polymers directly but they may be dehydrogenated or cracked to olefins.[3] Polymerization reactions are exothermic and occur at low temperatures, while pyrolysis reactions are endothermic and require high temperatures, so that in general a two-stage treatment is required when paraffin hydrocarbons are used. As a result of their experiments, Sullivan, Ruthruff and Kuentzel[4] have concluded that one-step processes are inferior to the two-step for these hydrocarbons. However, Keith and Ward,[5] in their work on the Unitary (one-stage) process, do not agree with this observation and state that the one-step process may be used advantageously with paraffins, under the proper conditions. These investigators also present evidence to show that direct reaction of saturated and unsaturated molecules may and does occur under these circumstances.[6]

From free energy calculations it can be shown that olefins are unstable below about 425°C. Below this temperature these hydrocarbons tend to polymerize, and isomerization of the higher members of the series to the corresponding naphthenes is also possible.[7] Cracking of olefin hydrocarbons to lower molecular weight hydrocarbons generally takes place above 425°C. The products usually obtained may be classified as (1) olefin polymers and naphthenes, (2) higher olefins, paraffins, naphthenes and polynaphthenes and (3) aromatics (resulting from secondary reactions). These three types result by treatment at progressively higher temperatures.

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[1] Such processes are discussed in Chapters 13, 14, 16 and 22. Also, Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, **1934**.

[2] G. Egloff, *Nat. Pet. News*, 1935, **27** (47), 25; *Chem. Abs.*, 1936, **30**, 3212; *J. Inst. Pet. Tech.*, 1936, **22**, 52A.

[3] In this connection it is of interest to note that A. D. Petrov (*Khim. Tverdogo Topliva*, 1934, **5**, 632; *Brit. Chem. Abs.* **B**, 1936, 52; *Chem. Abs.*, 1935, **29**, 3503) has noted that under the influence of electrical discharges, paraffins, naphthenes and aromatics will undergo polymerization. See Chapter 9.

[4] F. W. Sullivan Jr., R. F. Ruthruff and W. E. Kuentzel, *Ind. Eng. Chem.*, 1935, **27**, 1072; *Chem. Abs.*, 1935, **29**, 7627; *Brit. Chem. Abs.* **B**, 1935, 979.

[5] P. C. Keith, Jr. and J. T. Ward, *Oil Gas J.*, 1935, **34** (28), 36; *Refiner*, 1936, **14**, 506; *J. Inst. Pet. Tech.*, 1936, **22**, 155A; *Chem. Abs.*, 1936, **30**, 3211.

[6] For reviews on polymerization see: G. Egloff, *Nat. Pet. News*, 1935, **27** (47), 25; *Chem. Abs.*, 1936, **30**, 3212; *J. Inst. Pet. Tech.*, 1936, **22**, 52A. W. W. Gary, *World Petroleum*, 1935, **6**, 622; *Chem. Abs.*, 1935, **29**, 8306. M. Friedwald, *Rev. petrolifère*, **1935**, 1531; *Chem. Abs.*, 1936, **30**, 2355. P. P. Shoruigin, *Trans. VI Mendeleev Congr. Theoret. Applied Chem.* (1932), 1935, **2** (1), 762; *Chem. Abs.*, 1936, **30**, 2548. A. Dunstan, E. N. Hague and R. V. Wheeler, *Chaleur & ind.*, 1934, **15** (167), 402; *Chem. Abs.*, 1934, **28**, 6557; *Ind. Eng. Chem.*, 1934, **26**, 307; *Chem. Abs.*, 1934, **28**, 6557; *Brit. Chem. Abs.* **B**, 1934, 486. B. A. Kazanskii, *Uspekhi Khim.*, 1934, **3**, 116; *Chem. Abs.*, 1934, **28**, 5400. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**; and "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**.

MECHANICS OF POLYMERIZATION

Polymerization is a composite process, and the development of a complex molecule must require a series of consecutive reactions.[8] The latter may be regarded from two viewpoints, that is, either as a series of step-wise reactions or a chain mechanism.[9] In the first of these hypotheses, a substance is thought to polymerize primarily to the dimer, which then reacts with another molecule to form the trimer, which in turn unites with another monomer to give the tetramer, and so on. On the fundamental assumption that the rates of the consecutive polymerization reactions are not greater than that of the dimerization, Chalmers shows that the dimer and other low polymers (such as trimer and tetramer) would be formed in the largest amounts. However, this is not the case, as higher polymers normally predominate in the product. Furthermore, the reaction course of the monomer does not follow this proposed step-wise system. Chalmers, therefore, rejects this view and in its stead adopts a chain mechanism. The reaction chain is conceived as a primary activation of the monomer and a subsequent process of concatenation[10] which is rendered possible by the presence of free terminal bonds in all of the intermediate stages. The linking of the monomeric bonds initially proceeds at a rate which is almost instantaneous compared with that of the activation, but for very great chain lengths the speed becomes increasingly slow.

Gee and Rideal[11] consider polymerization to be a chain reaction in which the chains are broken by the operation of a steric factor (due to the arrangement of the molecules in space). According to this view the growth of chains may be terminated in several ways, as for instance (1) spontaneous deactivation, (2) by collision with a molecule of a monomer and (3) by partial deactivation. The importance of steric hindrance has been shown by Gee[12] who found that the proportion of the olefin polymerized before the maximum reaction velocity is attained varies from zero, with a strong deactivation, to 0.33 with no deactivation and zero steric factor, and finally approaches a value of 0.5 for large steric factors.

Dostal and Mark[13] look upon the mechanism as proceeding in two definite steps, the first of which is the formation of nuclei by collision of two monomeric molecules. This reaction requires an energy of activation and may be either uni- or bi-molecular. The second stage, rapid compared with the first, involves the growth of chains which may occur and be modified in a variety of ways. Applying this theory to the polymerization of styrene gave results in agreement with experimental observations.

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[7] A. R. Bowen and A. W. Nash. *World Petroleum Congr., London*, 1933, Proc. 2, 774; *Chem. Abs.*, 1934, **28**, 3865; *Brit. Chem. Abs.* **B**, 1934, 744; *J. Inst. Pet. Tech.*, 1934, **20**, 94A.

[8] Reviews on the mechanics of polymerization are given by: G. Egloff, *Nat. Pet. News*, 1935, **27** (47), 65; *J. Inst. Pet. Tech.*, 1936, **22**, 51A; *Chem. Abs.*, 1936, **30**, 3212. M. Stoll, *Trans. Faraday Soc.*, 1936, **32**, 1031; *Chem. Abs.*, 1936, **30**, 6271. A. S. C. Lawrence, *Science Progress*, 1934, **29**, 244; *Chem. Abs.*, 1934, **28**, 7096. Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. G. Egloff, "The Reactions of Pure Hydrocarbons," Reinhold Publishing Corp., New York, 1937.

[9] W. Chalmers, *J.A.C.S.*, 1934, **56**, 912; *Brit. Chem. Abs.* **A**, 1934, 607; *Chem. Abs.*, 1934, **28**, 3060.

[10] Concatenation refers to a union occurring in a chain-like series.

[11] G. Gee and E. K. Rideal, *Trans. Faraday Soc.*, 1935, **31**, 969; *Chem. Abs.*, 1935, **29**, 7162; *Brit. Chem. Abs.* **A**, 1935, 1080.

[12] G. Gee. *Trans. Faraday Soc.*, 1936, **32**, 656; *J. Inst. Pet. Tech.*, 1936, **22**, 263A; *Chem. Abs.*, 1936, **30**, 4380; *Brit. Chem. Abs.* **A**, 1936, 570.

[13] H. Dostal and H. Mark. *Z. physik. Chem.*, 1935, **29B**, 299; *Trans. Faraday Soc.*, 1936, **32**, 54; *Chem. Abs.*, 1935, **29**, 7162; *Brit. Chem. Abs.* **A**, 1936, 295.

A mechanism based upon the theories of free radicals and electronegativities has been proposed by Kline and Drake.[14] The two free radicals formed by the scission of a molecule are designated as positive and negative. Thus, (1) trimethylethylene behaves as if it were activated as:

$$(1)\quad (CH_3)_2C{=}CHCH_3 \longrightarrow \overset{-}{C}H_3 + CH_3\overset{+}{C}{=}CHCH_3$$

These two fragments then add to the double bond[15] of a non-activated molecule to form 3,4,5,5-tetramethylhexene-2,

$$(2)\quad \overset{-}{C}H_3{-}CH_3\overset{+}{C}{=}CHCH_3 + (CH_3)_2\overset{+}{C}{=}\overset{-}{C}HCH_3 \longrightarrow CH_3C(CH_3)_2CHCH_3CCH_3{=}CHCH$$

or may combine with the isomer to form 3,5,5-trimethylheptene-2,

$$(3)\quad \overset{-}{C}H_3{-}CH_3\overset{+}{C}{=}CHCH_3 + CH_3CH_2\overset{+}{C}CH_3{=}\overset{-}{C}H_2 \longrightarrow CH_3CH_2C(CH_3)_2CH_2CCH_3{=}CHCH_3$$

Both of these substances have been isolated in the condensation products of trimethylethylene. The same mechanism has also been applied to isobutene polymerization. From a consideration of the relative strengths of the carbon-hydrogen and carbon-carbon bonds, it may be expected that isobutene would have more of a tendency to split into negatively charged methyl and positively charged isopropenyl radicals than into positive hydrogen atoms and negative isobutenyl radicals. The products obtained in the polymerization can be accounted for on the basis that about 80 per cent of the molecules were activated in the first manner (giving rise to 2,4,4-trimethylpentene-1) and 20 per cent following the second (resulting in 2,4,4-trimethylpentene-2).

Catalysts. An application of thermodynamics to a reaction will indicate whether or not that reaction is thermodynamically possible at a certain temperature and pressure, and what the maximum yield will be at equilibrium. However, due to the fact that time is not a thermodynamic variable, this science furnishes no means of foretelling how long a duration will be required for equilibrium to be established.[16] In most polymerization reactions the velocity is extremely slow, so that equilibrium may be brought about only after several days. Since catalysts accelerate the speed of reaction and often bring about the transformations in an extremely short interval, the application of these agents to this field has become widespread.[17]

It should be borne in mind, however, that catalysts cannot increase the maximum thermodynamic yield; they merely speed up the rate of reaction to reach that condition in a shorter time. Catalysts may be selective, that is, exhibit definite preference for the acceleration of one reaction while not affecting, or perhaps even inhibiting, others in the same system.

There are two possibilities as to the mechanism of catalysis, according to Gee and Rideal.[18] The catalyst may initiate a chain center or it may form a reactive complex. The second view is considered the more probable one by these investigators, as it explains most experimental observations with reasonable exactitude. On the other hand the first is true only in a relatively small number of instances. In catalytic treatment the assumption that the velocity of a polymerization reaction and the size of the polymers produced diminish in the same ratio is shown to be not strictly accurate. Nevertheless, this is a good approximation in the early stages of reaction.

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[14] G. M. Kline and N. L. Drake, *Bur. Standards J. Research*, 1934, 13, 705; *Chem. Abs.*, 1935, 29, 1057; *J. Inst. Pet. Tech.*, 1935, 21, 90A; *Brit. Chem. Abs.* A, 1935, 192.

[15] The polarizability of the ethylene bond has been discussed by G. Wittig (*Ber.*, 1936, 69, 471; *Chem. Abs.*, 1936, 30, 3290).

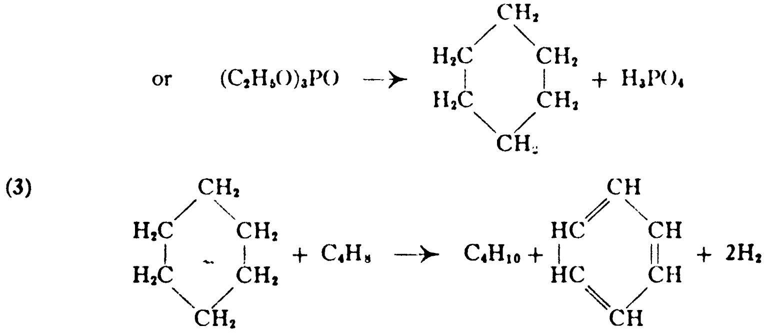
[16] G. S. Parks and S. S. Todd, *Ind. Eng. Chem.*, 1936, 28, 418; *Chem. Abs.*, 1936, 30, 3401; *Brit. Chem. Abs.* A, 1936, 701; *J. Inst. Pet. Tech.*, 1936, 22, 253A.

[17] The usefulness of catalysts in polymerization reactions has been discussed by A. E. Dunstan and D. A. Howes, *J. Inst. Pet. Tech.*, 1936, 22, 347; *Chem. Abs.*, 1936, 30, 6541; *J. Inst. Pet. Tech.*, 1936, 22, 352A; *Brit. Chem. Abs.* B, 1936, 915.

Phosphoric acid is one of the most common accelerators used for catalytic polymerizations. Ipatieff and Pines[19] explain the action of aqueous phosphoric acid as follows: (1) the formation of phosphate esters, (2) the decomposition of these esters to yield polymerides and naphthenes, (3) the dehydrogenation of naphthenes to aromatics and (4) the hydrogenation of olefins to paraffins by nascent hydrogen from the naphthenes. Using ethylene as the hydrocarbon, these reactions may be illustrated as:

$$\begin{array}{lrcl} (1) & C_2H_4 + H_3PO_4 & \longrightarrow & (C_2H_5O)H_2PO_3 \\ \text{or} & 2C_2H_4 + H_3PO_4 & \longrightarrow & (C_2H_5O)_2HPO_2 \\ \text{or} & 3C_2H_4 + H_3PO_4 & \longrightarrow & (C_2H_5O)_3PO \end{array}$$

$$(2) \qquad (C_2H_5O)_2HPO_2 \longrightarrow C_4H_8 + H_3PO_4$$



At temperatures below 200°C. the various phosphoric and phosphorous acids,[20] oxyhalides and acid esters of phosphorus[21] have all been recommended. It is often advantageous to use the phosphoric acid catalyst in a "solid" form in which siliceous adsorbents (e.g., kieselguhr or fuller's earth) are impregnated with the acid[22] or mixed with cadmium acid phosphate.[23] In aqueous solution, phosphoric acid may also be employed in conjunction with other acids, such as boric acid,[24] or with metallic salts,[25] especially of silver and copper.[26] Sulphuric acid may be substituted[27] but at lower operating temperatures,[28] especially when tertiary olefins are involved.[29] The latter acid has been suggested[30] for the conversion to liquid fuels of mixtures of olefins obtained by the dehydration of alcohols produced by the catalytic reduction of carbon monoxide under pressure (the so-called "Synthol" reaction).[31]

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[18] G. Gee and E. K. Rideal, *Trans. Faraday Soc.*, 1936, **32**, 666; *J. Inst. Pet. Tech.*, 1936, **22**, 263A; *Chem. Abs.*, 1936, **30**, 4384; *Brit. Chem. Abs.* **A**, 1936, 570.

[19] V. N. Ipatieff and H. Pines, *Ind. Eng. Chem.*, 1935, **27**, 1364; *Chem. Abs.*, 1936, **30**, 275; *Brit. Chem. Abs.* **A**, 1936, 51.

[20] V. N. Ipatieff, U. S. P. 1,960,631, May 29, 1934, to Universal Oil Products Co.; *Chem. Abs.*, 1934, **28**, 4587; *Brit. Chem. Abs.* **B**, 1935, 295; *J. Inst. Pet. Tech.*, 1934, **20**, 458A. Also Canadian P. 353,253, 1935; *Chem. Abs.*, 1935, **29**, 8316. Ortho-, meta-, pyro- and hypo-phosphoric acids and ortho-, hypo- and pyro-phosphorous acids are included.

[21] French P. 790,945, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 2985.

[22] V. N. Ipatieff, U. S. P. 1,993,512 and 1,993,513, May 5, 1935, 2,018,065 and 2,018,066, Oct. 22, 1935, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1936, 438; *Chem. Abs.*, 1935, **29**, 2546; *J. Inst. Pet. Tech.*, 1935, **21**, 219A; *Chem. Abs.*, 1936, **30**, 109, 281; *Brit. Chem. Abs.* **B**, 1936, 730. This is often referred to as the "U.O.P." (Universal Oil Products) catalyst.

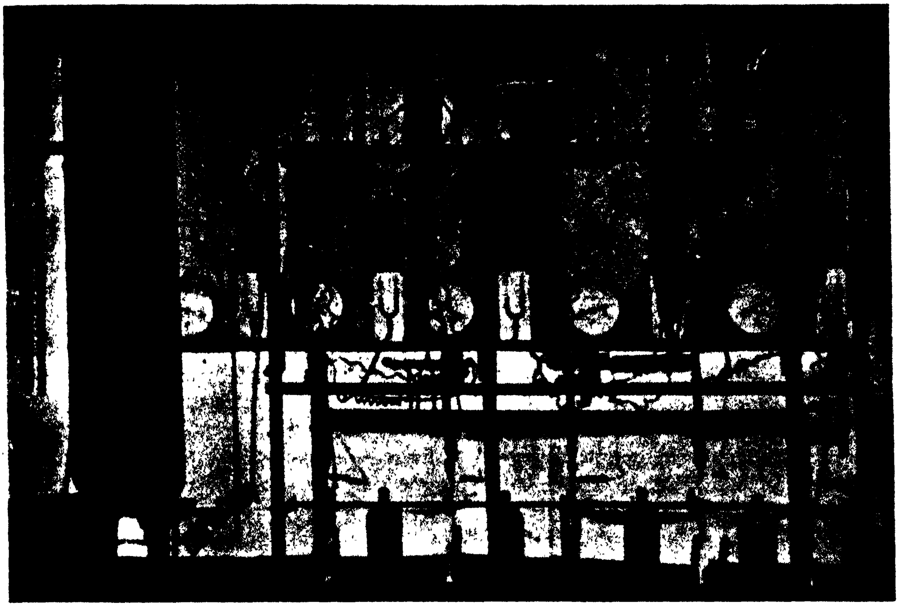
[23] A. E. Dunstan and D. A. Howes, *J. Inst. Pet. Tech.*, 1936, **22**, 347; *Chem. Abs.*, 1936, **30**, 6541; *J. Inst. Pet. Tech.*, 1936, **22**, 352A; *Brit. Chem. Abs.* **B**, 1936, 915.

[24] H. Plauson, German P. 600,002, 1934; *Chem. Abs.*, 1934, **28**, 6443.

[25] V. N. Ipatieff, U. S. P. 2,020,649, Nov. 12, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 484; *J. Inst. Pet. Tech.*, 1936, **22**, 23A.

[26] British P. 447,973, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 7120; *J. Inst. Pet.*

In addition to the acids mentioned, various metallic halides have been reported as being effective for the polymerization. Egloff has stated that pure, anhydrous aluminum chloride appears to be inactive, and that it is only in the presence of minute traces of moisture (and therefore hydrochloric acid) that this substance acts catalytically.[32] High-molecular-weight polymers may be obtained with boron trifluoride charged with hydrofluoric acid, phosphorus tri- or pentafluoride at



Courtesy Journal of Institution of Petroleum Technologists

Fig. 141.—Experimental Units for Catalytic Polymerization of Olefins. (A. E. Dunstan and D. A. Howes)

Tech., 1936, **22**, 352A. British P. 450,592 and 450,668, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 451A; *Brit. Chem. Abs.* **B**, 1936, 971; *Chem. Abs.*, 1936, **30**, 109.

[27] J. C. Morrell and G. Egloff, *Oil Gas J.*, 1934, **32** (45), 51; *Chem. Abs.*, 1934, **28**, 4579; *J. Inst. Pet. Tech.*, 1934, **20**, 321A.

[28] V. N. Ipatieff, U. S. P. 2,039,799, May 5, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 4175.

[29] W. Engs and R. Moravec, U. S. P. 2,007,159 and 2,007,160, July 9, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 5456; *Brit. Chem. Abs.* **B**, 1936, 632, 917. Also Canadian P. 340,308, 1934; *Chem. Abs.*, 1934, **28**, 3740.

[30] British P. 448,690, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 7837; *Brit. Chem. Abs.* **B**, 1936, 778; *J. Inst. Pet. Tech.*, 1936, **22**, 401A. French P. 790,873, 1936; *Chem. Abs.*, 1936, **30**, 3206. See also British P. 456,315, 1936, to Standard Alcohol Co.; *J. Inst. Pet. Tech.*, 1937, **23**, 20A.

[31] See Chapter 52. Also Carleton Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., Inc., New York, 1930.

[32] G. Egloff, *Nat. Pet. News*, 1935, **27** (47), 65; *Chem. Abs.*, 1936, **30**, 3212; *J. Inst. Pet. Tech.*, 1936, **22**, 52A. A discussion of reactions with aluminum chloride has been given in Chapter 6.

temperatures below —10°C. in the presence of an inert solvent[33] or with disubstituted boron fluorides (dihydrated, dialcoholated or diacetylated).[34] The use of nickel, iron and titanium chlorides[35] and fused zinc chloride at high temperatures[36] has also been suggested.

Clay mixed with diatomaceous earth,[37] nickel oxide,[38] or activated carbon[39] is sometimes used. Carbon monoxide[40] in the presence of nickel mixed with aluminum oxide has been reported as being very active. Oxygen also exerts a catalytic effect,[41] most likely due to the formation of an intermediate oxide which decomposes giving a bivalent radical of one or more carbon atoms.

ETHYLENE

Storch[42] investigated the kinetics of the polymerization of ethylene at 377°C. and 1415 mm. pressure with heating times of 1 to 3 hours. Butene is the primary product and propene evidently a secondary one. Minute traces (0.02 per cent) of oxygen doubled the reaction rate, and because of the difficulty of entirely removing this element from ethylene, reproducible rates of polymerization could not be obtained. The addition of ethyl mercaptan (0.1 per cent concentration) decreased the rate about tenfold. However, in the latter case the speeds were duplicable within about 5 per cent.[43] Evidence obtained shows that the reaction is not a simple bimolecular process. The energy of activation is given as 43,500 cal. Investigations by Krauze, Nemtzov and Soskina[44] showed that at 315-380°C. with high ethylene concentrations, the reaction is practically homogeneous and of a bimolecular nature. No catalytic action was imparted by iron, nickel, copper, chromium, zinc oxide or activated carbon. Rapid polymerization is said to result at 300°C., however, if azomethane is introduced in small amounts.[45]

By contacting ethylene with boron trifluoride and a promoter such as nickel embedded on a carrier, good yields of butene may be obtained at 8 to 10°C. and 50 atmospheres pressure at relatively short contact times. Longer periods of contact yielded almost exclusively liquid products.[46]

Polymerization of ethylene in the presence of phosphoric acid at 250-300°C. and 50 to 65 atmospheres pressure, according to Ipatieff and Pines, furnishes a mixture of paraffinic, olefinic, naphthenic and aromatic hydrocarbons. On the other hand, thermal treatment of the olefin under the same conditions gives no aromatics and only small percentages of paraffins.[47] There is no evidence of cracking in the catalytic treatment. Table 130 lists the boiling ranges of the liquid products formed by the catalytic operation. From measurements of the indices of refraction and densities, the concentration of paraffins was believed to be greatest in the lowest boiling fractions, while aromatics predominated in those boiling above 225°C. Naphthenes were present in the fractions above 110°C. An interesting observation was that isobutane was formed to the extent of 2.5 per cent at 250°C. and 18.8 per cent at 330°C. (based on the weight of ethylene reacting). The presence of isobutane is attributed to isomerization of the 1- or 2-butene (formed during polymerization) to isobutene and subsequent hydrogenation of the latter. At slightly higher temperatures (300-360°C. and 60 atmospheres pressure) with a "solid" phosphoric acid catalyst (H_3PO_4 embedded on kieselguhr) the reaction is said to be 80 to 85 per cent complete, with about 90 per cent of the product being liquid.[48] The phosphoric acid catalyst was found to be equally effective when the contact material was used in the solid form or suspended in a liquid medium (the synthetic oil, Kogasin II[49] was the dispersing agent).

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[33] British P. 401,297, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 2367; *Brit. Chem. Abs.* **B**, 1934, 136.

[34] French P. 793,226, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 4514. British P. 453,854, 1936; *Brit. Chem. Abs.* **B**, 1936, 1191; *J. Inst. Pet. Tech.*, 1936, **22**, 544A.

[35] C. R. Wagner, U. S. P. 1,934,896, Nov. 14, 1933, to Pure Oil Co.; *Chem. Abs.*, 1934, **28**, 631; *Brit. Chem. Abs.* **B**, 1934, 790.

[36] J. C. Morrell, U. S. P. 2,039,440 and 2,039,441, May 5, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 4314; *J. Inst. Pet. Tech.*, 1936, **22**, 307A.

[37] M. Halpern, W. B. Logan, R. E. Manley and W. Ullrich, Canadian P. 342,155, 1934, to Texaco Development Corp.; *Chem. Abs.*, 1934, **28**, 5655.

[38] E. J. Houdry, U. S. P. 2,035,478, Mar. 31, 1936; *Chem. Abs.*, 1936, **30**, 3622; British P. 421,650, 1934, to Houdry Process Corp.; *Brit. Chem. Abs.* **B**, 1935, 215; *J. Inst. Pet. Tech.*, 1935, **21**, 99A; W. F. Faragher and E. J. Houdry, Canadian P. 353,825, 1935, to Houdry Process Corp.; *Chem. Abs.*, 1936, **30**, 2747.

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[40] P. K. Frolich, U. S. P. 2,002,534, May 28, 1935, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1936, 583; *Chem. Abs.*, 1935, **29**, 4373.

[41] G. Egloff, *Nat. Pet. News*, 1935, 27 (45), 65; *Chem. Abs.*, 1936, **30**, 3212; *J. Inst. Pet. Tech.*, 1936, **22**, 52A.

[42] H. H. Storch, *J.A.C.S.*, 1934, **56**, 374; *Chem. Abs.*, 1934, **28**, 2252; *Brit. Chem. Abs.* **A**, 1934, 369; *J. Inst. Pet. Tech.*, 1934, **20**, 239A.

[43] H. H. Storch, *J.A.C.S.*, 1935, **57**, 2598; *Chem. Abs.*, 1936, **30**, 2084; *Brit. Chem. Abs.* **A**, 1936, 164; *J. Inst. Pet. Tech.*, 1936, **22**, 87A.

[44] M. V. Krauze, M. S. Nemtzov and E. A. Soskina, *Compt. rend. acad. sci., U.R.S.S.*, 1934, **2**, 301; *Chem. Abs.*, 1934, **28**, 5320; *Brit. Chem. Abs.* **A**, 1934, 736.

[45] O. K. Rice and D. V. Sickman, *J.A.C.S.*, 1935, **57**, 1384; *Chem. Abs.*, 1935, **29**, 5729; *Brit. Chem. Abs.* **A**, 1935, 1084.

[46] M. Otto and L. Bub, U. S. P. 1,989,425, Jan. 29, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1835.

TABLE 130.—*Boiling Ranges of Liquid Products Obtained by Polymerization of Ethylene with Phosphoric Acid at 50 to 65 Atmospheres Pressure.*

Polymerization Temperature, °C.	Percentage of Total Liquid Product Below 110°C.	 110-225°C.	 225-300°C.	 Above 300°C.
250	37	26	27	10
280	31	33	23	13
300	42	20	26	12
333	46	14	29	11

Malishev[50] has investigated the polymerization of ethylene using a catalyst composed of equal parts of phosphoric anhydride and lampblack. Under 65 atmospheres pressure, the rate of the reaction was quite slow at room temperature, but at 110°C., a rapid fall of pressure occurred. The reaction was completed at 260°C. after a 2-hour period of heating. About 40 per cent of the ethylene was converted into a liquid boiling between 20° and 240°C. containing olefins, paraffins, aromatics and naphthenes. Malishev believed that phosphoric anhydride is a more active catalyst for polymerizations than is phosphoric acid, and is somewhat similar to aluminum chloride in its action.

Egloff and Schaad have shown that polymerization of ethylene takes place more readily in a static than in a dynamic system.[51] Employing an autoclave at 50 atmospheres pressure, a 63 to 73 per cent conversion to liquids was obtained at 380°C. With a steel tube, however, a temperature of 420°C. was required for the same yield at 50 atmospheres pressure. Butadiene and paraffins up to nonane were found in the product. Aluminum oxide exerted very little catalytic action, but when a mixture of the oxides of nickel, aluminum and copper was employed as a catalyst at 330°C., an explosion resulted giving carbon, hydrogen and methane.

Conversion of ethylene to liquid fuels by thermal treatment has been investigated by Sullivan, Ruthruff and Kuentzel.[52] In their experiments, carried out in high pressure bombs at temperatures of 370 to 455°C., the interdependence of the three variables, temperature, pressure and time of contact, was very clearly shown. In this series of tests, during the initial heating period the ethylene was introduced into the bomb at a low rate of flow. When the operating temperature was reached, the flow was increased to a predetermined value, after which all conditions were maintained as constant as possible. At very high pressures, conversion to liquids increased very rapidly with increasing time of contact up to a maximum, after which cracking of the polymer occurred. In Table 131 are summarized the conditions for maximum polymer yield and the effect of pressure on the reaction.

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[47] V. N. Ipatieff and H. Pines, *Ind. Eng. Chem.*, 1935, **27**, 1364; *Chem. Abs.*, 1936, **30**, 275; *J. Inst. Pet. Tech.*, 1936, **22**, 18A; *Brit. Chem. Abs.* **B**, 1936, 51. *J. Gen. Chem (U.S.S.R.)*, 1936, **6**, 321; *Chem. Abs.*, 1936, **30**, 6321. *Nat. Pet. News*, 1936, **28** (9), 30; *J. Inst. Pet. Tech.*, 1936, **22**, 201A.

[48] K. Peters and K. Winzer, *Brennstoff-Chem.*, 1936, 17, 366; *Brit. Chem. Abs.* **B**, 1936, 1139.

[49] See Chapter 52 for a discussion of the properties of Kogasin II.

[50] B. W. Malishev, *Petroleum Z.*, 1936, **32**, (19), 1; *Brit. Chem. Abs.* **B**, 1936, 677; *Chem. Abs.*, 1936, **30**, 7988.

[51] G. Egloff and R. E. Schaad, *J. Inst. Pet. Tech.*, 1933, **19**, 800; *Brit. Chem. Abs.* **B**, 1933, 1046; *Chem. Abs.*, 1934, **28**, 94.

[52] F. W. Sullivan, Jr., R. F. Ruthruff and E. E. Kuentzel, *Ind. Eng. Chem.*, 1935, **27**, 1072; *Chem. Abs.*, 1935, **29**, 7627; *Brit. Chem. Abs.* **B**, 1935, 929.

TABLE 131.—*Effect of Pressure on the Thermal Polymerization of Ethylene.*

Pressure lbs./sq. in.	Temperature °F.	Time of Contact Min.	Liquid Yield %	Gravity of Liquid °API	Gasoline Boiling Below 390°F. %	Octane No. of Gasoline
500	850	8.1	59.1	49.0	73.8	78
1000	850	27.4	70.0	49.3	69.5	68
2000	850	22.4	80.8	48.0	62.5	64
3000	700	85.0	75.0	46.5	40.2	62
3000	750	43.0	74.8	47.5	47.3	63
3000	800	17.3	74.3	47.7	55.0	62
3000	850	9.6	71.4	50.1	67.1	63

An investigation covering pressures of 34 to 90 atmospheres at temperatures of about 400°C. was conducted by Smolenski and Kowalewski.[53] In their procedure, ethylene under pressure was very slowly heated up to the operating temperature (requiring about 5 hours). This precaution is quite important, because under these pressures if the ethylene is heated too rapidly an explosion will occur (resulting in the formation of methane and carbon). The polymerization was then carried out by maintaining the gas at 400°C. for 2 to 2.5 hours. This treatment resulted in an almost complete conversion to liquid products which ranged from hydrocarbons of the gasoline fraction to those of lubricating oils, depending upon the pressure employed. The yields of the various fractions are listed in Table 132. The portions boiling up to 250°C. were refined by treatment with sulphuric acid and subsequently washed with water and sodium hydroxide, removing 20 to 25 per cent of unsaturated and aromatic hydrocarbons. The refined liquids contained mainly paraffins with slight amounts of naphthenes. Hydrogenation of the crude product under 90-100 atmospheres pressure diminished the yield from 92 to 75-80 per cent of liquid product, which contained 15 to 20 per cent of unsaturates.

TABLE 132.—*Liquid Products from Non-Catalytic Polymerization of Ethylene at 400°C.*

Pressure, atmospheres	34	51	90
Yield of crude liquid, %	80	92	97
Density, 20°C.	0.764	0.775	0.792

Fractions from Distillation of Crudes
(Per Cent of Total Volume)

Below 150°C.	45.6	29.5	19.5
150-250°C.	39.6	42.5	28.5
275-300°C.	6.0	6.6	6.8
Over 300°C.	8.2	21.0	43.5

The reduction in yield is attributed to rupture of long chains and the subsequent hydrogenation of the fragments. Further experimentation showed that at 420°C. and pressures of 67-210 atmospheres depolymerization takes place, with the cyclization of olefins to give naphthenes and dehydrogenation of these substances to produce aromatics. Smolenski and Kowalewski point out that the chemical character of polymerization products depends more on the temperature than on the presence of a catalyst of the type of alumina. Liquid products may also be produced by passing ethylene over metal surfaces either coated or alloyed with tin, zinc, aluminum or chromium at 400 to 900°C.[54]

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[53] K. Smolenski and S. Kowalewski, *Bull. intern. acad. polonaise. Classe sci. math. nat.*, **1934A**, 315; *Chem. Abs.*, 1935, **29**, 1058; *Brit. Chem. Abs.* **A**, 1935, 191; *Przemysl. Chem.*, 1934, **18** (10-12), 547; *J. Inst. Pet. Tech.*, 1935, **21**, 132A; K. Smolenski, *Brennstoff-Chem.*, 1934, **15**, 212.

By heating lower olefins to 400-700°C. for short contact times (less than 2 seconds) in the presence of 0.5 to 1 per cent of oxygen in a reactor having a large volume-surface ratio, higher olefins are very readily produced. At 600°C. under these conditions, ethylene gives 59.3 per cent propene, 12.2 per cent butene and 28.4 per cent pentene.[55] No dissociation to carbon and hydrogen or excessive formation of methane or other paraffins is said to result at this temperature. Above 650°C., however, the polymers undergo cracking, which reduces the yield. The maximum degree of polymerization is reported to occur in the range of 550° to 650°C. using unpacked glass or metal tubes. The formation of carbon may be retarded by the addition of about 0.1 per cent of sulphur dioxide to the gas, which is then passed over a copper catalyst at 450-750°C.[56] The introduction of nascent hydrogen into the mixture of ethylene and sulphur dioxide prior to catalytic treatment has also been proposed to avoid the production of unsaturated liquid hydrocarbons.[57]

PROPENE

The kinetics of the polymerization of propene at 330 to 400°C. have been investigated by Krauze, Nemtzov and Soskina.[58] The reaction progressed in a manner analogous to that of ethylene, and is apparently of the second order kinetically. The activation energy is calculated to be 37,400 cal., and the variation of the equilibrium constant with the temperature is given by:

$$\log_{10} k = 10.23 - \frac{8320}{T}$$

Liquid orthophosphoric acid is a very effective catalyst for the polymerization of propene at temperatures as low as 130°C. At moderate conditions (135 to 200°C. and 1 to 15 atmospheres pressure), this hydrocarbon is said to be capable of transformation into a liquid consisting almost entirely of iso-structure monolefins, such as hexenes, nonenes, dodecenes and pentadecenes. At higher temperatures and pressures and with longer contact times, naphthenes, aromatics and paraffins also result.[59] At 330 to 370°C. and high pressure, the degree of unsaturation of the products is much greater in the catalytic than in the thermal treatment. The types of hydrocarbons formed are the same, except that in the latter case, cycloparaffins and cycloölefins predominate, while aromatics are absent. Table 133 gives the approximate percentage composition of the products obtained by the thermal and catalytic polymerization of propene.[60]

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[54] F. Winkler and H. Hauber, German P. 593,248, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 3078.

[55] S. Lenher, U. S. P. 2,000,964, May 14, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 4373; *J. Inst. Pet. Tech.*, 1936, **22**, 53A. British P. 432,430, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 893; *Chem. Abs.*, 1936, **30**, 484.

[56] F. Eisenstecken, German P. 588,158, 1933; *Chem. Abs.*, 1934, **28**, 1353.

[57] F. Eisenstecken, German P. 589,914, 1933; *Chem. Abs.*, 1934, **28**, 2363.

[58] M. V. Krauze, M. S. Nemtzov and E. A. Soskina, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 343; *Chem. Abs.*, 1935, **29**, 6204; *Brit. Chem. Abs.* **A**, 1935, 1081; *Compt. rend. acad. sci. U.R.S.S.*, 1934, **3**, 262; *Chem. Abs.*, 1935, **29**, 113; *Brit. Chem. Abs.* **A**, 1934, 1179.

[59] V. N. Ipatieff, *Ind. Eng. Chem.*, 1935, **27**, 1067; *Brit. Chem. Abs.* **B**, 1935, 1035; *Chem. Abs.*, 1935, **29**, 7935; *J. Inst. Pet. Tech.*, 1935, **21**, 408A.

TABLE 133.—*Polymerization Products of Propene at 330-370°C. and High Pressure.*

Composition	Thermal	Phosphoric Acid Catalyst
Paraffins, %	8	15
Olefins, %	26	63
Cycloparaffins, %	44	10
Cycloölefins, %	22	6
Aromatics, %	0	6

According to Sullivan, Ruthruff and Kuentzel[61] propene does not yield as large a conversion to liquid fuels as ethylene under the same conditions of thermal polymerization. However, the specific gravity of the liquid, percentage boiling in the gasoline range and the octane number of this gasoline fraction are all much higher than with the ethylene polymer. The optimum results are given in Table 134, which also shows the effect of high pressure treatment.

TABLE 134.—*Effect of Pressure on the Thermal Polymerization of Propene.*

Pressure lbs./sq. in.	Temperature °F	Time of Contact Min.	Liquid Yield %	Gravity of Liquid °API	Gasoline Range Boiling Below 390°F. %	Octane No. of Gasoline
500	850	5.7	16.3	53.2	80.3	78
1000	800	22.6	46.9	53.6	73.1	87
2000	800	16.9	64.0	53.4	69.5	75
2000	850	10.6	62.8	49.8	66.2	80
3000	750	27.3	62.6	52.7	59.5	75
3000	800	16.4	61.0	52.5	63.4	74
3000	850	8.7	61.2	50.3	67.1	74

Brandes, Gruse and Lowy[62] have studied low temperature polymerization of propene using zinc chloride carried on pumice stone. The effect of this catalyst can be seen from Table 135.

TABLE 135.—*Polymerization of Propene.*

Temperature, °C.	Pressure lb./sq. in.	Time of Contact Min.	Yield of Liquid %	Sp. Gr. Liquid
With Zinc Chloride Catalyst				
290-300	1600	90	74.2	0.7571
200-208	2050	60	43.5	0.7491
150-160	3400	360	64.4	0.7441
Without Catalyst				
290-308	2475	92	4.3	0.7665
200-215	2150	60	0.3	—
150-160	3350	360	0.2	—

Without the presence of the zinc chloride, practically no liquids were obtained, other conditions being approximately the same. Examination of the polymers showed that the chief constituents were olefins and paraffins, together with some naphthenes in the higher fractions. Complete absence of aromatic hydrocarbons was noted, however. The hydrocarbons produced are listed according to their carbon content in Table 136.

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[60] V. N. Ipatieff and H. Pines *Ind. Eng. Chem.*, 1936, **28**, 684; *J. Inst. Pet. Tech.*, 1936, **22**, 306A; *Chem. Abs.*, 1936, **30**, 8145.

[61] F. W. Sullivan, Jr., R. F. Ruthruff and W. E. Kuentzel, *Ind. Eng. Chem.*, 1935, **27**, 1072; *Chem. Abs.*, 1935, **29**, 7627; *Brit. Chem. Abs.* **B**, 1935, 979.

[62] O. L. Brandes, W. A. Gruse and A. Lowy. *Ind. Eng. Chem.*, 1936, **28**, 554; *J. Inst. Pet. Tech.*, 1936, **22**, 256A; *Chem. Abs.*, 1936, **30**, 4147; *Brit. Chem. Abs.* **A**, 1936, 819.

TABLE 136.—*Liquid Products Obtained from the Pressure Treatment of Propene Using a Zinc Chloride Catalyst.*

Operating Temp. °C.	Chief Constituents Present, Per Cent by Volume C_5	C_6	C_7	C_8	C_9	C_{10-12}	Per Cent Distilling in Gasoline Range (to 200°C.)
290-310	5.8	10.1	5.9	12.9	18.7	27.3	74.5
200-210	0.07	7.0	1.6	2.0	47.0	32.0	85.9
150-160	0.3	10.6	1.2	1.7	55.9	24.1	92.0

Oxygen in a concentration of 0.5 to 1.0 per cent favors the production of higher olefins from propene. The optimum conditions are given as 550° to 650°C., pressures up to 15 atmospheres and reaction times less than 2 seconds. At temperatures above 650°C., decomposition to carbon, hydrogen and paraffins is also noted, as in the case of ethylene. At 600°C. in the presence of 0.5 per cent oxygen, using a reactor having a large volume-surface relation, the following unsaturated hydrocarbons are formed: 9.3 per cent butene, 27.4 per cent pentene, 32.3 per cent hexene, and 30.4 per cent higher olefins b.p. 74-100°C.[63]

BUTENES

Polymerization reactions of 2-butene and isobutene are homogeneous and of the second order, according to Krauze, Nemtzov and Soskina. The velocity constants at 370°C. are governed by the equations

$$\log_{10} k = 10.0 - \frac{38,000}{2.3RT}$$

$$\text{and} \qquad \log_{10} k = 12.3 - \frac{43,000}{2.3RT}$$

respectively (R is the gas constant and T is the absolute temperature). As a general rule, the velocity constant decreases rapidly with increase in molecular weight in the case of the normal olefins, while the existence of two chains attached to the double bond increases the rate, as in isobutene.[64]

The calculations of Parks and Todd on the free energy change for the formation of diisobutylene from isobutene following the reaction

$$2C_4H_8 \text{ (gas)} \rightleftharpoons C_8H_{16} \text{ (liquid)}$$

give $\Delta F°$ of −6,930 cal. at 298°K. (25°C.). This negative value for the free energy change means that the reaction may be expected to proceed spontaneously from left to right, since the equilibrium constant is related to the change in free energy by the equation:

$$\Delta F° = -2.3RT \log K$$

It is of interest to note the approximate temperature limitations deduced by thermodynamics for this reaction. On the assumption that the free energy change may be expressed as a linear function of the absolute temperature (which is equivalent to taking the difference in the specific heats of the products and the reactants equal to zero), it can be shown that the above reaction is not possible at ordinary pressure above 402°K. (129°C.).[65]

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[63] British P. 432,430, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 893; *Chem. Abs.*, 1936, **30**, 484.

[64] M. V. Krauze, M. S. Nemtzov and E. A. Soskina, *Compt. rend. acad. sci., U.R.S.S.*, 1934, **3**, 262; *Brit. Chem. Abs.* **A**, 1934, 1179; *Chem. Abs.*, 1935, **29**, 113.

Ipatieff and Corson found that the rate of polymerization of the butenes using aqueous phosphoric acid as catalyst increased in the order 1-butene, 2-butene and isobutene. The liquid polymerization products are similar in physical and chemical properties, all being mixtures of liquid monolefins. Mild conditions (30°C.) favor the formation of only two simple polymers (dimer and trimer). At higher temperatures, as many as seven compounds were obtained from isobutene, however diisobutene and triisobutene were the predominant resultants.[66]

In addition to polymerization, phosphoric acid causes considerable isomerization with the butenes.[67] For this reason Ipatieff and Corson point out the fact that there may be doubt as to the reliability of the relative rates of polymerization that they reported. For instance, although the starting hydrocarbons were pure specimens, the material which was actually polymerized might have been a mixture of the isomeric butenes, the relative amounts of which would depend upon the experimental conditions. In the light of this, isobutene was observed to accelerate the polymerization of the *n*-butenes, while the latter affected the rate of polymerization of propene in the same manner. Sulphuric acid is particularly effective in selectively polymerizing isobutene to di- or to di- and triisobutylene from mixtures of olefins.[68]

Hydrocarbons of high molecular weight are produced from isobutene by the action of volatile metallic halides. Temperatures from —10° to about 50°C. are reported as effective when using beryllium chloride, zinc chloride, phosphorus pentafluoride, arsenic trifluoride, osmium octafluoride, boron trichloride, stannic chloride, titanium tetrachloride and antimony pentafluoride.[69] By means of boron trifluoride, isobutene may be polymerized at —15°C. to compounds having a molecular weight of 10,000-15,000. With a specially purified isobutene, treated with this promoter at —80°C., the molecular weight of the product may be increased to as high as 40,000.[70] In this connection it is interesting to note that treatment with aluminum chloride[71] at temperatures of —78° to 16°C. gives rise to olefins and cyclic products of molecular weights in the range of only 132 to 4800.[72]

Various silicates, such as silica gel and fuller's earth, render maximum catalytic effect after being activated at a temperature between 300° and 325°C.[73] According to Lebedev and Borgman[74] the factors of contact time, temperature and method of activation of the catalyst determine the yields and degree of complexity of the products. Activated floridin in contact with 2-butene at room temperatures for 1, 2 and 4 months produced 45-50, 60 and 80-85 per cent polymerization, respectively.[75'] The product consisted of 43 per cent of the dimer, 15-18 per cent of the trimer and the remainder higher polymers.

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[65] G. S. Parks and S. S. Todd, *Ind. Eng. Chem.*, 1936, **28**, 418; *Chem Abs.*, 1936, **30**, 3401; *Brit. Chem. Abs.* **A**, 1936, 701.

[66] V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, 1935, **27**, 1069; *J. Inst. Pet. Tech.*, 1935, **21**, 408A; *Chem. Abs.*, 1935, **29**, 7935.

[67] V. N. Ipatieff, H. Pines and R. E. Schaad, *J.A.C.S.*, 1934, **56**, 2696; *J. Inst. Pet. Tech.*, 1935, **21**, 47A; *Brit. Chem. Abs.* **A**, 1935, 192. See also C. Matignon, H. Moureu and M. Dode, *Bull. soc. chim.*, 1935, (5) **2**, 1169, 1181; *Brit. Chem. Abs.* **A**, 1935, 958; *Chem. Abs.*, 1935, **29**, 6567.

[68] French P. 794,397, 1936, to International Hydrogenation Patents Co. Ltd.; *Chem. Abs.*, 1936, **30**, 4510. See also G. A. Kramer, U. S. P. 1,953,618, Apr. 3, 1934, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 3740; *Brit. Chem. Abs.* **B**, 1935, 138.

[69] British P. 421,118, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 3353; *Brit. Chem. Abs.* **B**, 1935, 182; *J. Inst. Pet. Tech.*, 1935, **21**, 100A.

[70] British P. 432,196, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 109; *Brit. Chem. Abs.* **B**, 1935, 893.

[71] See Chapter 6 for a discussion of this catalyst.

[72] H. I. Waterman, J. Over and A. J. Tulleners, *Rec. trav. chim.*, 1934, **53**, 699; *Brit. Chem. Abs.* **A**, 1934, 864; *Chem. Abs.*, 1934, **28**, 5397; *J. Inst. Pet. Tech.*, 1934, **20**, 454A.

[73] Y. M. Slobodin, *J. Applied Chem.* (*U.S.S.R.*), 1935, **8**, 35; *Chem. Abs.*, 1935, **29**, 6709; *Foreign Petroleum Tech.*, 1935, **3**, 427; *J. Inst. Pet. Tech.*, 1936, **22**, 97A; *Brit. Chem. Abs.* **A**, 1935, 942.

[74] S. V. Lebedev and Yu. A. Borgman, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 1589; *Brit. Chem. Abs.* **A**, 1936, 702; *Chem. Abs.*, 1936, **30**, 2169.

Lebedev and Borgman show that the molecular weight of the polymers increases uninterruptedly with falling temperature. At —65°C. floridin (activated at 200°C.) gives rise to compounds varying from 112 to 12,000 in molecular weight. The polymers of isobutene produced at —70°C. consisted of 3.4 per cent octene, 20.7 per cent dodecene ($C_{12}H_{24}$), 15.3 per cent hexadecene ($C_{16}H_{32}$), 10.8 per cent tetracosene ($C_{24}H_{48}$), 5.4 per cent octacosene ($C_{28}H_{56}$), and 44.4 per cent higher hydrocarbons.[76] The action of alumina precipitated on silica gel yields similar monolefins from isobutene, substances up to the tetramer being detected.[77]

HIGHER OLEFINS

Pentenes. The normal pentenes have been shown by Waterman and coworkers to cyclicize very readily in the presence of aluminum chloride.[78] Experiments with 2-pentene using this catalyst at low temperatures (0° to —80°C.) yielded partly cyclic compounds, some having a molecular weight of 350 and containing only a mono ring formation.[79] At 400°C. with or without aluminum oxide, the cyclic character of the polymerization products is augmented.[80] Isopentenes, such as methylethylethylene, trimethylethylene and isopropylethylene, using aluminum chloride at 85°C. and 200°C. and alumina at 400°C. yielded partly cyclic substances. Dimers formed about 20 to 25 per cent of the product.[81]

Hexenes. The thermal polymerization of 2-hexene and 3-methyl-2-pentene has been investigated by Nemtzov and Poletaev,[82] who report that both reactions are of the second order kinetically. The rate of polymerization of the normal hexene is about twice that of the branched isomer, and is considerably lower than that of ethylene and propene condensations. The chief component of the reaction mixture in each instance is the dimer, with little trimer and no higher polymers. According to these investigators, 2-hexene is more stable than isohexene, but olefins are much more easily decomposed by thermal treatment than the corresponding paraffins. The normal hexenes begin to polymerize above 350°C. in the presence of molybdenum sulphide. At 400°C. this reaction becomes quite marked, yielding principally higher boiling hydrocarbons. Considerable isomerization to 2-hexene was noted. Only small amounts of 3-hexene and no isohexene could be detected.[83]

Laughlin, Nash and Whitmore have studied the equilibrium mixture of three of the isomeric hexenes. Tetramethylethylene, methylisopropylethylene and *ter*-butylethylene, heated to 300°C., were each passed over a catalyst of silica gel impregnated with phosphorus pentoxide. The product obtained from these treat-

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[75] S. V. Lebedev and S. M. Orlov, *J. Gen. Chem. (U.S.S.R.)*, 1935, **5**, 1589; *Chem. Abs.*, 1936, **30**, 2169; *Brit. Chem. Abs.* **A**, 1936, 702.

[76] S. V. Lebedev and Yu. A. Borgman, *loc. cit.*

[77] H. I. Waterman, J. J. Leendertse and A. J Kok, *Rec. trav. chim.*, 1934, **53**, 1151; *Chem. Abs.*, 1935, **29**, 2504; *Brit. Chem. Abs.* **A**, 1935, 192.

[78] See Chapter 6.

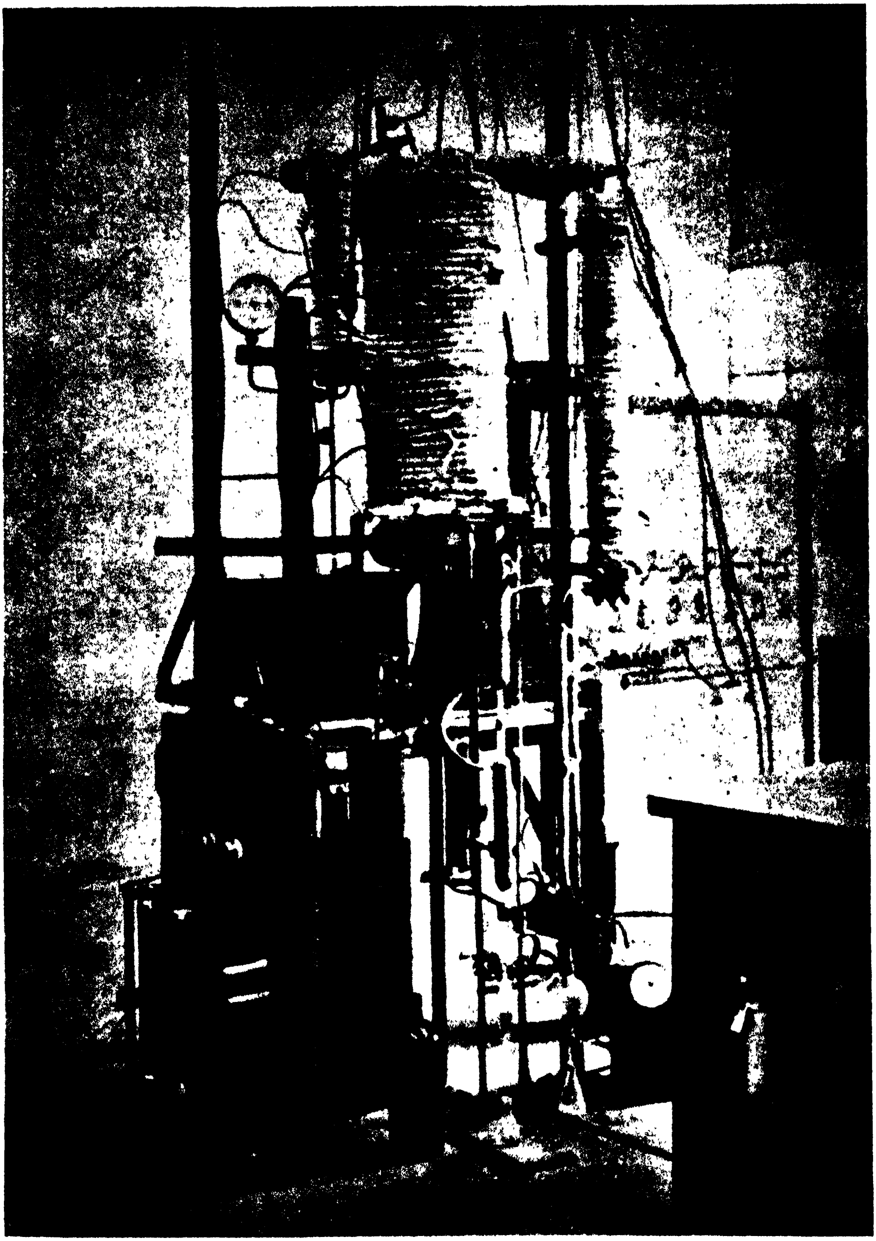
[79] H. I. Waterman and J. J. Leendertse, *Trans. Faraday Soc.*, 1936, **32**, 251; *Chem. Abs.*, 1936, **30**, 2457; *Brit. Chem. Abs.* **A**, 1936, 310. *Rec. trav. chim.*, 1935, **54**, 139; *Chem. Abs.*, 1935, **29**, 2803; H. I. Waterman, J. J Leendertse and I de Hulster, *J. Inst. Pet. Tech.*, 1935, **21**, 952; *Chem. Abs.*, 1936, **30**, 2735; *Brit. Chem. Abs.* **A**, 1936, 186; *J. Inst. Pet. Tech.*, 1936, **22**, 18A.

[80] H. I. Waterman, J. J. Leendertse and W. W. Klazinga, *Rec. trav. chim.*, 1935, **54**, 79; *Chem. Abs.*, 1935, **29**, 2503; *J. Inst. Pet. Tech.*, 1935, **21**, 161A.

[81] H. I. Waterman, J. J. Leendertse and J. P. Makkink, *J. Inst Pet. Tech.*, 1936, **22**, 333; *Chem. Abs.*, 1936, **30**, 5773; *Brit. Chem. Abs.* **A**, 1936, 961.

[82] M. S. Nemtzov and A. V. Poletaev, *J. Gen. Chem. (U.S.S.R.)*, 1936, **6**, 892; *Chem. Abs.*, 1936, **30**, 6701.

[83] A. D. Petrov, A. P. Meshcheriakov and D. N. Andreev, *Ber.*, 1935, **68**, 1; *Chem. Abs.*, 1935, **29**, 2145; *Brit. Chem. Abs.* **A**, 1935, 324.



Courtesy Journal of Institution of Petroleum Technologists

FIG. 142.—Experimental Catalytic Polymerization Plant. (A. E. Dunstan and D. A. Howes)

ments was a mixture of three isomers, and in each instance had the composition 61 per cent tetramethylethylene, 31 per cent *unsym*-methylisopropylethylene and 3 per cent *ter*-butylethylene. It is interesting to note that a mixture having the identical percentage composition results from the dehydration of methyl-*ter*-butyl carbinol (pinacolyl alcohol) with the same catalyst at 300°C.[84]

Cyclohexene. Cyclohexene may be converted into cyclohexyl-cyclohexene to the extent of 80 to 90 per cent by boiling with phosphorus pentoxide in a Soxhlet extractor.[85] Orthophosphoric acid also may be used, but is not as effective as the anhydride, and metaphosphoric acid (HPO_3) is without action.[86] Using aluminum chloride as a catalyst and liquid pentane as a diluent, Waterman, Leendertse and ter Poorten[87] observed that hardly any polymerization of cyclohexene took place at −78°C., and even at 40°C. the reaction was only slight, whereas with isobutene and isopropylethylene, reaction was quite violent at these temperatures. At 70°C., however, cyclohexene will polymerize quite readily giving high molecular weight cyclic products.[88]

Other Olefins. Activated floridin at 150-270°C. causes considerable isomerization of the tertiary butyl radical in the higher olefins. *ter*-Butylethylene underwent 47.4 per cent change to tetramethylethylene, and *unsym*-methyl-*ter*-butylethylene yielded 54 per cent of trimethylethylethylene. Neither of the products was affected by the floridin.[89] This catalyst may also exert a depolymerizing effect on higher olefins. At 50°C., triisobutylene begins to break down, and at 180° to 190°C. the decomposition is complete, 99 per cent being dissociated to diisobutylene and isobutene and the remainder to isobutane and octene. At the same time, part of the diisobutylene is repolymerized to form the tetramer and higher forms.[90]

To a small extent, pinene vapor is polymerized to polyterpenes at 330°C. in the presence of copper, nickel, cobalt and iron. The principal reaction at this temperature, however, is one of isomerization.[91]

POLYMERIZATION OF OLEFIN MIXTURES TO AROMATICS, AND LOW-BOILING LIQUID OLEFINS

Birch and Hague obtained yields of 5 per cent of styrene, 2 per cent of indene and some butadiene and cyclopentadiene by polymerization of the gaseous olefins resulting from the pyrolysis (at 850°C. and 20 lbs. per sq. in. pressure) of a still gas containing mainly methane, ethane, propane and butane. Styrene was believed to result from the union of ethylene and benzene, and subsequent dehydrogenation, as:

$$C_6H_6 + C_2H_4 \longrightarrow C_6H_5C_2H_5 \longrightarrow C_6H_5C_2H_3 + H_2$$

Indene may be formed by the combination of propene and benzene or toluene and ethylene, followed by ring closure and elimination of hydrogen, similar to the above reaction, or by demethanation of dicyclopentadiene:

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[84] K. C. Laughlin, C. W. Nash and F. C. Whitmore, *J.A.C.S.*, 1934, **56**, 1395; *Chem. Abs.*, 1934, **28**, 4372; *Brit. Chem. Abs.* A, 1934, 866.

[85] R. Truffault, *Compt. rend.*, 1935, **200**, 406; *Chem. Abs.*, 1935, **29**, 2927; *Brit. Chem. Abs.* A, 1935, 480.

[86] R. Truffault, *Bull. soc. chim.*, 1936, (v) **3**, 442; *Brit. Chem. Abs.* A, 1936, 598; *Chem. Abs.*, 1936, **30**, 3806.

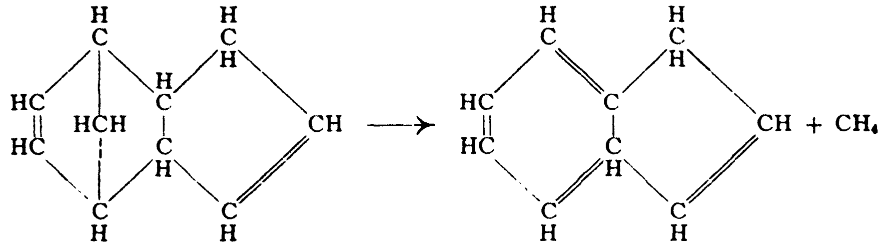
[87] H. I. Waterman, J. J. Leendertse and A. C. ter Poorten, *Rec. trav. chim.*, 1935, **54**, 245; *Chem. Abs.*, 1935, **29**, 2803; *Brit. Chem. Abs.* A, 1935, 480.

[88] H. I. Waterman and J. J. Leendertse, *Trans. Faraday Soc.*, 1936, **32**, 251; *Chem. Abs.*, 1936, **30**, 2457.

[89] S. V. Lebedev and N. A. Kudryavtzev, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 1859; *Chem. Abs.*, 1936, **30**, 3402; *Brit. Chem. Abs.* A, 1936, 702.

[90] S. V. Lebedev and I. A. Livshitz, *J. Gen. Chem.* (*U.S.S.R.*), 1934, **4**, 13; *Chem. Abs.*, 1934, **28**, 5398; *Brit. Chem. Abs.* A, 1934, 864.

[91] P. Sabatier, A. Mailhe and G. Gaudion, *Compt. rend.*, 1919, **168**, 926; *J.C.S.*, 1919, **116** (1), 336; *Chem. Abs.*, 1919, **13**, 1838. See also G. Egloff, M. Herrman, B. L. Levinson and M. F. Dull, *Chem. Rev.*, 1934, **14**, 287; *Chem. Abs.*, 1934, **28**, 5426.



Dehydrogenation or demethanation account for the formation of butadiene and cyclopentadiene.[92] Dunstan, Hague and Howes reported high yields of liquids by polymerizing ethylene hydrocarbons obtained from the thermal decomposition of mixtures of the lower paraffins. Polymerization was carried out in an autoclave at 100 atmospheres pressure and 380° to 410°C. In addition to styrene, indene and the diolefins mentioned above, benzene, toluene, *m*- and *p*-xylene, naphthalene, anthracene, phenanthrene and chrysene were produced.[93]

Low-boiling unsaturated liquids are formed by passing an "ethylene concentrate" (a mixture of lower olefins) through a quartz tube charged with silica gel and heated to 550-580°C. at atmospheric pressure.[94] An increase in temperature causes a higher yield of benzene at the expense of the olefins. Under pressure and at 320° to 360°C., using zinc chloride as the catalyst, the products are quite different, consisting of paraffins, aromatics, naphthenes and olefins, although the latter do not exceed 30 per cent in this case.

Both liquid products and acetylene may be recovered from waste gases such as those obtained in oil cracking, according to Morrell,[95] who recommends a three-step process. First the gas mixture is pyrolyzed at 800-1200°C. at reduced pressure and contact times of less than 0.10 second, to form high yields of olefins. The second step involves polymerization of these unsaturates (principally the propene and higher members of the series) to liquids by means of a phosphoric acid catalyst. The residual gases from this treatment (mostly ethylene) are now heated to about 1100°C., under reduced pressure, for about 0.10 second to produce acetylene. Morrell cites as an example a stabilizer gas containing 25 per cent methane, 23 per cent ethane, 18 per cent propane, 12 per cent butane and higher paraffins, 5 per cent hydrogen and 17 per cent olefins. This material was cracked at 900°C. and 50 mm. pressure for 0.01 second, and the resulting olefins polymerized at 400°F. and 100 lbs. per sq. in. pressure. The liquid obtained netted 3 gallons of gasoline per 1000 cu. ft. of input gas. The residual gas, heated to 1400°C. at a pressure of 50 mm. for 0.06 second gave 450 l. of acetylene per 1000 l. of the original stabilizer gas.

Ipatieff and Nemtzov[96] found that polymerization of mixtures of the lower olefins, such as ethylene and propene, was greatly influenced by the presence of hydrogen, since under these conditions a product resulted which boiled almost entirely below 200°C. Evidently, polymerization under these conditions is accompanied by hydrogenation to the corresponding paraffins. As a matter of fact, mixtures of ethylene and a large excess of hydrogen treated in a similar manner were found to give no liquid products, showing that hydrogenation predominated over polymerization. Although the gas mixture underwent polymerization above 350°C., it appears that saturation of the olefins occurs at much lower temperatures. Above 440°C. cracking begins to take place, as is shown by the deposition of carbon on the walls of the reaction vessel. Activated carbon and alumina were ineffective as catalysts. The carbonaceous material promoted the condensation reactions, however. The optimum conditions for the production of low-boiling liquid products are reported as a temperature slightly above 400°C. and a hydrogen pressure of 300 atmospheres.

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[92] S. F. Birch and E. N. Hague, *Ind. Eng. Chem.*, 1934, **26**, 1008; *Chem. Abs.*, 1934, **28**, 6982; *Brit. Chem. Abs.* **B**, 1934, 1049.

[93] A. E. Dunstan, E. N. Hague and D. A. Howes, *Chimie et industrie*, 1935, **34**, 273; *J. Inst. Pet. Tech.*, 1936, **22**, 18A; *Brit. Chem. Abs.* **B**, 1935, 934.

[94] I. Z. Ivanov, *J. Applied Chem.* (*U.S.S.R.*), 1933, **6**, 103; *Chem. Abs.*, 1933, **27**, 5714; *Foreign Petroleum Tech.*, 1933, **1** (3), 71; *J. Inst. Pet. Tech.*, 1934, **20**, 416A; *Brit. Chem. Abs.* **B**, 1933, 612.

[95] J. C. Morrell, U. S. P. 2,030,070, Feb. 11, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 2362.

[96] V. N. Ipatieff and M. S. Nemtzov, *Khim. Tverdogo Topliva*, 1932, **3**, 707; *Chem. Abs.*, 1934, **28**, 5644; *Foreign Petroleum Tech.*, 1934, **2**, 247; *J. Inst. Pet. Tech.*, 1935, **21**, 50A; *Brit. Chem. Abs.* **B**, 1935, 7.

STYRENE AND OTHER ARYL SUBSTITUTED OLEFINS

Polystyrene, a highly polymerized form of styrene, may be produced by heating the latter with about 2.5 per cent of benzoyl peroxide. Yields of about 34 per cent have been obtained by Natelson, using this method.[97] Staudinger and Steinhofer[98] found by heating polystyrene for 6 hours at 310-350°C. and atmospheric pressure, it underwent depolymerization, giving 62.5 per cent styrene, 19.2 per cent distyrene, 3.8 per cent tristyrene, no tetrastyrene and 9.6 per cent residue. At 290 to 320°C., under reduced pressure, and with a 12-hour heating period, the yield of styrene was reduced, amounting to only 38.4 per cent. The dimer was present in the same proportion as in the first case (19.2 per cent), however, the amounts of tristyrene, tetrastyrene and the residue were increased to 23.0, 3.8 and 11.4 per cent respectively. These investigators reported that the dimer consisted of 1,3-diphenyl-3-butene and 1,3-diphenylpropane, while the trimer was composed of 1,3,5-triphenyl-5-hexene and 1,3,5-triphenylpentane. Polymerization of styrene is apparently a chain process, interrupted by a secondary change which occurs with increasing frequency as the rate of polymerization increases.[99]

From their studies of the properties, mechanism of formation and constitution of the polymers of styrene obtained using various catalysts, Risi and Gauvin[100] have advanced a theory pertaining to the nature of the secondary change noted by Staudinger and Steinhofer. After standing for several days in the dark with antimony pentachloride in benzene solution, styrene formed a resinous mass which was separated into 2 polymers, one melting at 60°C. and having a molecular weight of 636 and the other with a molecular weight of 1335 and a melting point of 90° to 92°C. Both substances were saturated, as was shown by their inability to add bromine. Similar saturated polymers were also isolated from polystyrene prepared by the method of Staudinger and Steinhofer[101] (using sulphuric acid as catalyst) and from Fittig-Erdmann[102] distyrene (1,3-diphenylbutene-1) when polymerized by means of stannic chloride. On the other hand, the distyrene of Stoermer[103] (2,4-diphenylbutene-2) was not affected by the latter catalyst, from which Risi and Gauvin suggest that this hydrocarbon is likewise completely saturated. These investigators also agree with Staudinger and Steinhofer in that the polymerization reactions are of the chain type and do not take place by stages. The secondary transformation which is believed to check the polymerization involves the cyclization of the intermediary unsaturated polystyrene into a saturated filamentary molecule terminated by a hydrindenic ring. This may be represented graphically for the dimerization by the reaction:

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[97] S. Natelson, *Ind. Eng. Chem.*, 1933, **25**, 1391; *J. Inst. Pet. Tech.*, 1935, **21**, 29A; *Brit. Chem. Abs.* **A**, 1934, 62. Benzoyl peroxide may be formed by dissolving oxygen in the liquid styrene and adding benzaldehyde.

[98] H. Staudinger and A. Steinhofer, *Ann.*, 1935, **517**, 35; *Chem. Abs.*, 1935, **29**, 4336; *Brit. Chem. Abs.* **A**, 1935, 740.

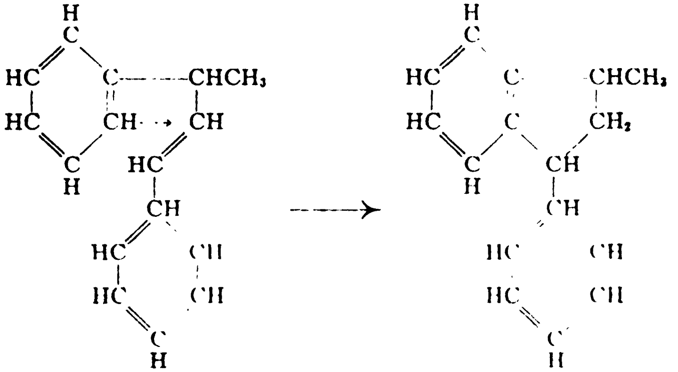
[99] See Carleton Ellis, "The Chemistry of Synthetic Resins." Reinhold Publishing Corp., New York, 1935, I, 232, for a discussion of the theories of polymerization of styrene.

[100] J. Risi and D. Gauvin, *Can. J. Research*, 1936, **14B**, 255; *Chem. Abs.*, 1936, **30**, 7549.

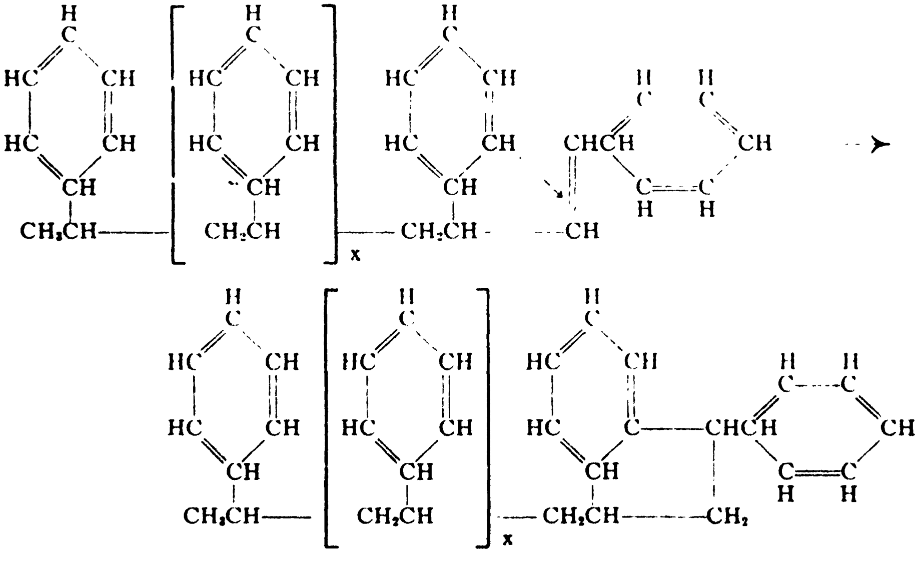
[101] H. Staudinger and A. Steinhofer, *loc. cit.*

[102] R. Fittig and E. Erdmann, *Ann.*, 1883, **216**, 179; *Chem. Zentr.* **1883**, 403; *J.C.S.*, 1883, **44**, 474.

[103] R. Stoermer and H. Kootz, *Ber.*, 1928, **61**, 2330; *Brit. Chem. Abs.* **A**, 1929, 55; *Chem. Abs.*, 1929, **23**, 1397.



Higher polymers may also be explained according to this system:



In contrast with the ease of combination of styrene molecules, propenylbenzene derivatives polymerize with difficulty, and only in the presence of catalysts. The introduction of a terminal methyl group diminishes the tendency of the ethylenic linkage toward combination to form complex molecules. Polymerization of propenylbenzene follows a chain mechanism with the linkages occurring in the 1,3 position (instead of the 1,2, as with other ethylenic compounds). This is probably due to the mobility of the hydrogen in the methyl group of the allyl radicals.[104]

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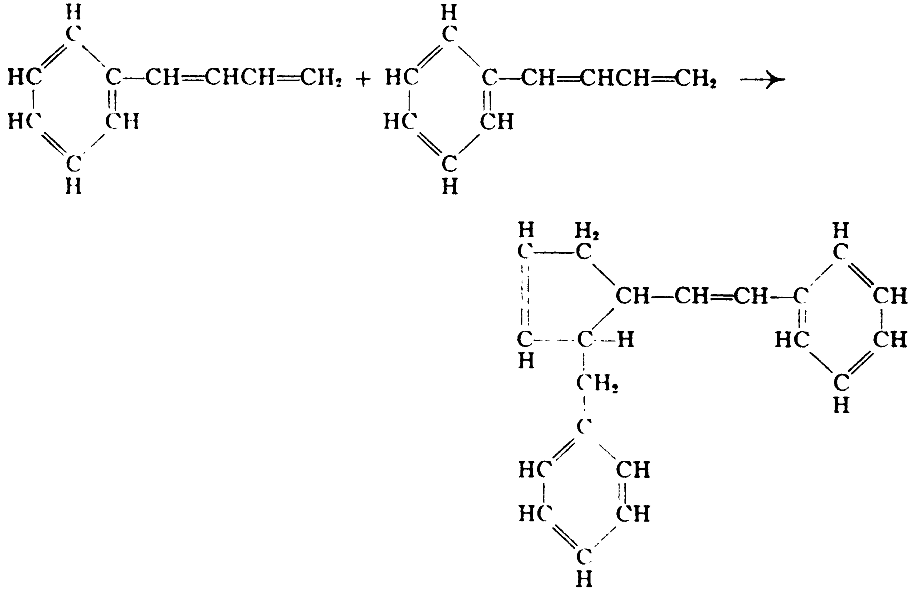
[104] H. Staudinger and E. Dreher, *Ann.*, 1935, 517, 73; *Chem. Abs.*, 1935, 29, 4336; *Brit. Chem. Abs.* A, 1935, 740.

Staudinger and Dreher polymerized propenylbenzene in toluene solution by means of boron trifluoride, the latter giving products having a molecular weight up to about 2000. Cracking of the polymer gave rise to diphenylbutadiene and propylbenzene.

Bergmann[105] found that 1-phenylbutadiene dimerizes to form 2-benzyl-1-styryl-3-cyclopentene. This result is explicable if the process is assumed to follow a course similar to that of the simple ethylenes[106] involving the formation of an open chain hydrocarbon by displacement of one hydrogen in the methylene group. Migration of one of the double bonds leads to the formation of a conjugated system in which one of the hydrogen atoms becomes activated and migrates with the formation of a five-membered ring, as for instance:



Phenylated olefins may be cyclicized into the corresponding tetralins or indanes by treating with 85-90 per cent sulphuric acid as a catalyst.[107] However, polymerization also occurs to a greater or less degree even with alcohols, which are dehydrated to the corresponding olefins in the presence of this promoter. Thus, 20 cc. of 1-phenylpentanol-1 (butyl phenyl carbinol) was added slowly, with constant stirring, to 30 cc. of 90 per cent sulphuric acid at 9 to 10°C. The olefin formed, 1-phenylpentene-1, was completely polymerized to a substance boiling at 163-165°C. at 2 mm. pressure. Similarly, 1-phenyl-2-methylpentanol-2, 3-phenylpropanol-1, 4-phenylbutanol-2, 4-phenyl-2-methylbutanol-2 and 4-phenylbutene-1 underwent considerable condensation with this catalyst.

DIOLEFINS

Allenes. Activated floridin causes a partial polymerization of hydrocarbons of the allene series. Methyl allene (1,2-butadiene) is polymerized to the extent of 22 per cent by passage over this catalyst at 245°C. and 25 per cent at 330°C. Dimers of methyl allene and also of bivinyl, the chief isomerization product,[108] could not be identified in the resulting polymers.[109] In the case of *unsym*-dimethyl allene [$CH_2{=}C{=}C(CH_3)_2$], however, the chief polymerization product was the dimer of isoprene. In fact, at temperatures above 334°C. using floridin activated at 325°C., the content of isoprene in the pyrolysis mixture remained unchanged, because the velocity of its formation is equal to that of its polymerization.[110]

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[105] E. Bergmann, *J.C.S.*, 1935, 1359; *Chem. Abs.*, 1936, 30, 88; *Brit. Chem. Abs.* A, 1935, 1497.

[106] F. C. Whitmore, *Ind. Eng. Chem.*, 1934, 26, 94; *Chem. Abs.*, 1934, 28, 1327; *J. Inst. Pet. Tech.*, 1934, 20, 79A.

[107] R. O. Roblin, Jr., D. Davidson and M. T. Bogert, *J.A.C.S.*, 1935, 57, 151; *J. Inst. Pet. Tech.*, 1935, 21, 90A; *Chem. Abs.*, 1935, 29, 1804.

Butadiene. The kinetics and mechanism of the thermal polymerization of 1,3-butadiene at 400-700°C. and atmospheric pressure were studied by Moor, Strigaleva and Shilyaeva.[111] Results of experiments made in a copper coil and a vertical porcelain tube indicate that at 400°C. the primary thermal reaction is bimolecular and may be represented by:

$$2C_4H_6 \longrightarrow C_8H_{12}$$

By polymerizing at 450-700°C. products of both higher and lower boiling points than butadiene are obtained. The change of surface has apparently no effect, as the two methods produced substantially equal results. The energy of activation under these conditions is given as 28,000 cal. per mole, while the variation of the rate with temperature is given by the expression:

$$\log_{10} k = 7.32 + \frac{6400}{T}$$

Rubanovskii used the glow discharge method to investigate the kinetics of butadiene polymerization.[112] At 0.001 to 0.1 mm., the pressure in the discharge tube increases to what corresponds to the cracking of butadiene, whereas above 0.1 mm. the pressure decreases because of the contraction in volume in the polymerization of the hydrocarbon. During discharge, in a mixture of hydrogen and butadiene, the shock impact of the hydrogen atom also is believed to induce polymerization. The chain character of the mechanism is indicated by the induction period (3 to 7 minutes, which is typical for this type of reaction). The acceleration of the rate of reaction by dilution with argon and oxygen, which hampers the diffusion and breaking of chains on the sides of the tube, further suggests the chain mechanism. In addition, the speed of polymerization is much greater in a larger tube. The kinetics of the process are not affected by the characteristics of the discharge nor by the material of the electrodes.

The thermal polymerization of liquid butadiene at 110-200°C. has been reported by Lebedev and co-workers to be a homogeneous reaction, greatly catalyzed by the presence of oxygen. The energy of activation for the liquid phase treatment is 13,000 cal. On the other hand, in order to have the reaction proceed in the gaseous phase over the same temperature range, an energy of activation of 25,000 cal. is required.[113]

Heating at 150°C. for 120 hours converts butadiene into a dimer, consisting mainly of 1-ethenyl-3-cyclohexene and a small amount of 1-ethenyl-1-cyclohexene. No open chain dimerides are formed, and there is no tendency to further polymerization.[114] Slobodin also reports the formation of 1-ethenyl-3-cyclohexene by heating butadiene to 400°C. in the presence of a dehydrogenation catalyst.[115] The dimer, 1-ethenyl-3-cyclohexene, is said to be the chief resultant of the thermal polymerization of butadiene in the presence of nitrogen at temperatures of 250 to 400°C. However, with long periods of contact, especially at high temperatures, hydrogen and methane were also formed, indicating decomposition of the polymers.[116] The addition of copper naphthenate or oleate in small percentages (0.001 to 0.41 per cent of copper) has been suggested to restrict the polymerization of butadiene to the dimer stage alone.[117] After heating butadiene for 29 days at 80°C. in the presence of 3.20 per cent of copper naphthenate (0.407 per cent copper), 45.87 per cent of dimer, but no higher polymers resulted. Metallic copper acts in a similar manner, but is less effective. Although an increase in the concentration of either copper or its salts increases the effectiveness for prevention of higher polymers, the dimerization reaction is stated to proceed independent of the concentration of the inhibitor.[118]

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[108] See Chapter 2.

[109] Y. M. Slobodin, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 48; *Brit. Chem. Abs.* **A**, 1935, 957; *Chem. Abs.*, 1935, **29**, 4732.

[110] Y. M. Slobodin, *J. Gen. Chem.* (*U.S.S.R.*), 1934, **4**, 778; *Chem Abs.*, 1935, **29**, 2145; *Brit. Chem. Abs.* **A**, 1935, 62.

[111] V. G. Moor, N. V. Strigaleva and L. V. Shilyaeva, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 818; *Chem. Abs.*, 1936, **30**, 365; *Brit. Chem. Abs.* **A**, 1936, 51. See also G. G. Koblyanskii and K. B. Piotrovskii, *Sintet Kauchuk*, **1936**, (3), 3; *Chem. Abs.*, 1936, **30**, 5069.

[112] L. Rubanovskii, *J. Phys. Chem.* (*U.S.S.R.*), 1933, **4**, 431; *Chem. Abs.*, 1934, **28**, 2980.

[113] S. V. Lebedev, M. A. Khokhlovkin, L. I. Kuibina and A. P. Begetova, *Sintet. Kauchuk*, **1936** (1), 2; *Chem. Abs.*, 1936, **30**, 4078.

Diazoaminobenzene has been suggested as a catalyst for polymerizing butadiene in the Russian synthetic rubber industry.[119] The process is carried out at 100°C. under 18-20 atmospheres pressure with constant stirring. Another catalyst which may be used for the polymerization is metallic sodium. However, it has been pointed out that the technical butadiene obtained from petroleum does not undergo polymerization with sodium because of the destruction of this catalyst by the admixed impurities.[120] The use of an alkali metal, such as sodium, in conjunction with an unsaturated ether (vinyl ethyl ether), is also recommended.[121] The polymerization of butadiene with sodium in an atmosphere of carbon dioxide has been investigated by Koblyanskii and Rokityanskii,[122] who report that under these conditions, the rate of polymerization is greatly retarded and a different type of polymer formed. The reaction product is described as a white porous substance, insoluble in benzene, chloroform and ether, containing 88.67 per cent carbon and 11.04 per cent hydrogen. It is stated to be autocatalytic to the polymerization reaction and also to oxidize quite rapidly on exposure to air. Alkali organic compounds of the type of sodium triphenylmethyl and sodium diphenylmethyl also catalyze polymerization.[123]

A method of removing butadiene from cracked gases has been suggested by Odell.[124] The gas mixture (such as refinery gas) is preheated to 300-800°F., mixed with hot combustion gases and about 0.5 per cent oxygen, 10 per cent steam and a small amount of sulphur dioxide and then passed over a bed of solid refractory material. The contact mass ordinarily employed is fire brick, into which may be also incorporated substances of a promoting nature, such as aluminum phosphate, iron oxide or aluminum oxide. The polymerization of butadiene and other unstable diolefins is said to be complete in about 1 to 5 seconds at temperatures of 600-1400°F. and pressures of 50 to 175 lbs. per sq. in. with this treatment.

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[114] S. V. Lebedev and S. Sergienko, *Compt. rend. acad. sci., U.R.S.S.*, 1935, **3**, 79; *J. Gen. Chem. (U.S.S.R.)*, 1935, **5**, 1839; *Brit. Chem. Abs.* **A**, 1935, 1480; 1936, 702; *Chem. Abs.*, 1936, **30**, 1023, 2548.

[115] Y. M. Slobodin, *J. Gen. Chem. (U.S.S.R.)*, 1935, **5**, 1415; *Chem. Abs.*, 1936, **30**, 2169.

[116] I. A. Volzhinskii, M. K. Zhegis, L. B. Rubina and M. S. Sheremet'eva, *Sintet. Kauchuk*, **1936** (1), 8; *Chem. Abs.*, 1936, **30**, 6757.

[117] A. I. Savel'ev, O. G. Arbidan and A. V. Zlatogurskii, *Sintet. Kauchuk*, **1936** (4), 18; *Chem. Abs.*, 1936, **30**, 7385.

[118] The rate of polymerization of butadiene is also lowered by the presence of various aliphatic and aromatic ketones and diketones, aldehydes and aliphatic and olefinic alcohols. See N. A. Chayanov and Z. N. Nemtsova, *Colloid J. (U.S.S.R.)*, 1936, **2**, 487; *Chem. Abs.*, 1937, **31**, 3329.

[119] M. A. Lur'e and V. A. Ignatyuk, *Sintet. Kauchuk*, **1932** (3), 12; *Chem. Abs.*, 1933, **27**, 6016; *Brit. Chem. Abs.* **B**, 1934, 232.

[120] N. Z. Andreev, A. N. Makashina and A. E. Mal'tzeva, *Sintet. Kauchuk* **1934** (3), 12; *Chem. Abs.*, 1935, **29**, 3976; *Brit. Chem. Abs.* **B**, 1936, 535. See also Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**.

[121] G. Ebert, F. A. Fries and P. Garbsch, U. S. P. 2,008,491, July 16, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 5855; *J. Inst. Pet. Tech.*, 1936, **22**, 53A.

[122] G. G. Koblyanskii and I. V. Rokityanskii, *Sintet. Kauchuk*, **1936** (6), 2; *Chem. Abs.*, 1936, **30**, 7385.

[123] K. Ziegler and L. Jakob, *Ann.*, 1934, **511**, 45; *Chem. Abs.*, 1934, **28**, 5431; *Brit. Chem. Abs.* **A**, 1934, 864.

[124] W. W. Odell, U. S. P. 1,925,151, Sept. 5, 1933; *Brit. Chem. Abs.* **B**, 1934, 663; *Chem. Abs.*, 1933, **27**, 5520. British P. 418,779, 1934; *Chem. Abs.*, 1935, **29**, 3143; *Brit. Chem. Abs.* **B**, 1935, 88.

Cyclopentadiene. The kinetics of the polymerization of cyclopentadiene have been investigated by Khambata and Wassermann[125] and Kistiakowsky and Mears.[126] The results of Khambata and Wassermann show that the reaction when carried out in a benzene solution at 15 to 55°C. is bimolecular.[127] Kistiakowsky and Mears studied the dimerization using tetrahydronaphthalene as solvent and also found the transformation to be of the second order, with about the same absolute rate as that in benzene solution. However with pure liquid cyclopentadiene, the latter authorities report that the order decreases, the reaction being nearly of the first order kinetically, with an activation energy of 17,300 cal.[128] In neither investigation was evidence obtained to indicate a chain mechanism for the dimerization.

The constitution of the polymerization products of cyclopentadiene is of a very complex nature. Pirsch supported the Diels and Alder theory[129] which postulates the formation of polymers of the isocamphene type. These conclusions were based on determinations of the molecular melting point depression of the various derivatives.[130] However, Alder and Stein[131] showed that the evidence of this nature was insufficient to prove the problems of structure and configuration. The latter investigators point out that the differences between the heats of hydrogenation of the various compounds could be due either to a strain in the molecule or to the particular structure of the bridged ring.[132] The later work of Alder and Stein[133] shows that the formation of these polymers consists of two reactions, first of the partial 1,4 addition of two conjugated unsaturated molecules and secondly of the addition of a conjugated system at the isolated double bond of the reaction product of the first stage as shown in reactions (1) and (2), respectively, on page 653. Thus, every one of the polymers is capable of adding another molecule of cyclopentadiene, and the formation of a continuous series of homologues is limited only by physical properties, according to Alder and Stein. For instance, the solubility of the polymers begins to decrease so rapidly at the tetracyclopentadiene that the polymerization is practically finished with the heptacyclopentadiene.

Barrett and Burrage[134] have measured the change in vapor pressure of the system during the polymerization of cyclopentadiene. From the vapor pressure-composition curve of known mixtures of cyclopentadiene and its dimer, the course of the reaction could be followed. After 93 days, at 12°C., the dimerization was

[125] B. S. Khambata and A. Wassermann, *Nature*, 1936, **137**, 496; *Brit. Chem. Abs.* **A**, 1936, 684; *Chem. Abs.*, 1936, **30**, 4078.

[126] G. B. Kistiakowsky and W. H. Mears, *J.A.C.S.*, 1936, **58**, 1060; *Chem. Abs.*, 1936, **30**, 5488; *J. Inst. Pet. Tech.*, 1936, **22**, 395A; *Brit. Chem. Abs.* **A**, 1936, 939.

[127] A. Wassermann (*Nature*, 1936, **138**, 369; *Chem. Abs.*, 1936, **30**, 7431) has reported that the reaction when carried out in paraffin solution is also bimolecular.

[128] According to B. S. Khambata and A. Wassermann (*Nature*, 1936, **138**, 368; *Chem. Abs.*, 1936, **30**, 7431), the decomposition of dicyclopentadiene to give cyclopentadiene is unimolecular both in paraffin solution and in the pure liquid state.

[129] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934, 651; also Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935, 831.

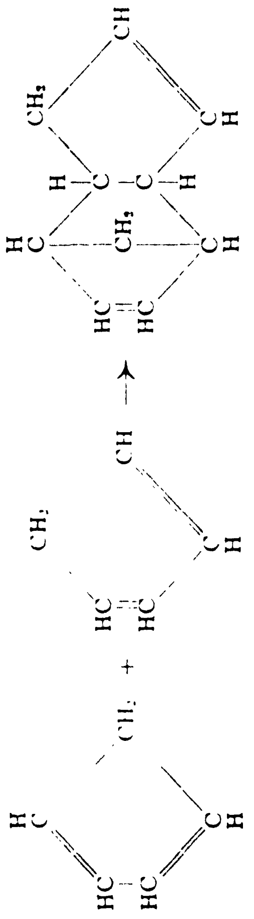
[130] J. Pirsch, *Ber.*, 1934, **67**, 101; *Chem. Abs.*, 1934, **28**, 2335; *Brit. Chem. Abs.* **A**, 1934, 285.

[131] K. Alder and G. Stein, *Ber.*, 1934, **67**, 373; *Chem. Abs.*, 1934, **28**, 3061; *Brit. Chem. Abs.* **A**, 1934, 517.

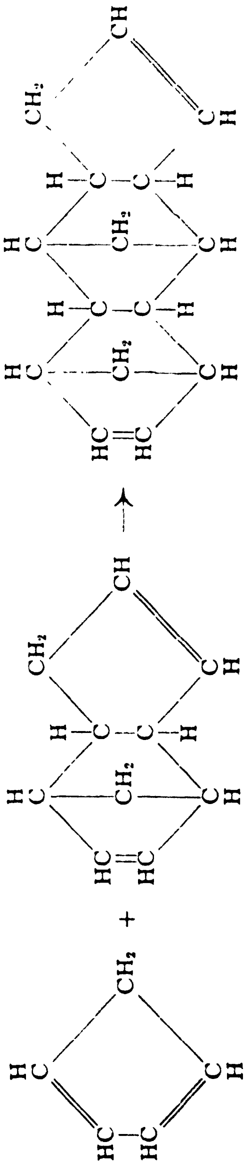
[132] K. Alder and G. Stein, *Ber.*, 1934, **67**, 613; *Chem. Abs.*, 1934, **28**, 6114; *Brit. Chem. Abs.* **A**, 1934, 641.

[133] K. Alder and G. Stein, *Angew. Chem.*, 1934, **47**, 837; *Chem. Abs.*, 1935, **29**, 2516; *Brit. Chem. Abs.* **A**, 1935, 203.

[134] E. G. V. Barrett and L. J. Burrage, *J. Phys. Chem.*, 1933, **37**, 1029; *Chem. Abs.*, 1934, **28**, 958; *J. Inst. Pet. Tech.*, 1934, **20**, 22A.



(1)



(2)

99.27 per cent. The transformation is apparently complete after one year. The refraction analysis method of Stobbe and Reuss[135] for determining the rate of polymerization (which is based on the simple dimerization process) has been proven to be in error by the work of Terent'ev and Solokhin.[136] Polymerization of the dimer to higher polymers causes increased values in the observed refractive indices. The disregard of the latter reactions causes considerable error in the degree of polymerization indicated by the refractometer observations.

POLYMER GASOLINE

Because of the increasing demand for high octane gasoline and the simultaneous recurring fear that crude oil supplies may become exhausted, much interest has been shown in the potential supply of motor fuel made possible by the polymerization of olefins. The requirements for greater quantities of gasoline were at first largely filled by the cracking process. Egloff[137] has pointed out that in 1934, cracking (of gasoline and heavy oil) supplied 300 billion cu. ft. of gases, one-sixth of which were olefins that could be polymerized to over 1 billion gal. of gasoline having an octane number of about 81. An additional 2 billion gal. of motor fuel of the same quality could be obtained by dehydrogenation and subsequent polymerization of the deolefinized gas. Refinery gases (from the distillation of crude oils) represented another billion gal. of potential gasoline had the propene and butane been dehydrogenated and polymerized, while the natural gas and gasoline industries added another 5 billion gal. in the form of propane and butane. Thus, the total polymerized gasoline potentially available in the United States alone in 1934 was over 9 billion gal. or about 50 per cent of the total gasoline consumed. The amount of crude oil required to produce the 1934 demand for gasoline would have been reduced to 60 per cent of its volume had this potential supply of polymer gasoline been utilized; or 360,000,000 barrels of crude oil could have been conserved in that year.

In addition to its high antiknock rating, polymer gasoline has a high octane blending value.[138] Comparison of these characteristics with those of benzol and isooctane are given in Table 137.

TABLE 137.—*Octane Ratings and Blending Values of Polymer Gasoline.*

	Octane Rating	Blending Value
Polymer gasoline	81	103-125
Benzol	97	84-91
Isooctane	100	94-99

There are two general divisions for the processes available for this type of polymerization,[139] one purely thermal, and the other catalytic. The first method utilizes still gases or natural gas and is essentially a two-step process, cracking the gas to olefins and subsequent polymerization of the latter by application of heat and pressure. The second procedure involves only polymerization of unsaturated hydrocarbons at relatively low temperatures and pressures in the presence of an accelerator, such as phosphoric acid.

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[135] H. Stobbe and F. Reuss, *Ann.*, 1912, **391**, 151; *Chem. Abs.*, 1912, **6**, 3275; *J.C.S.*, 1912, **102** (1), 842.

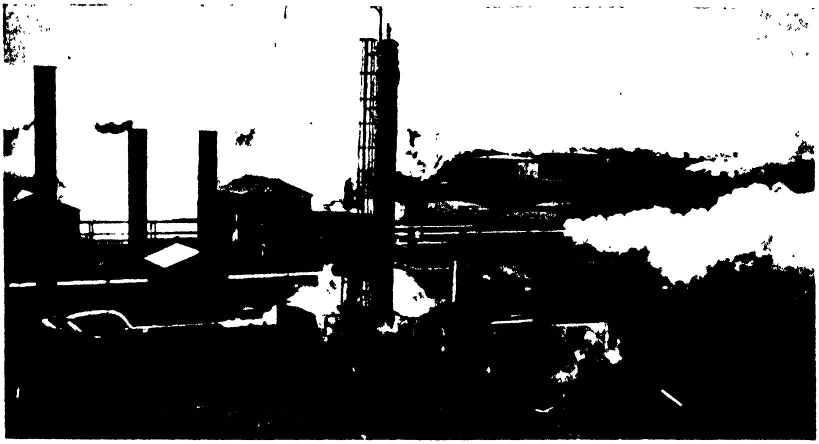
[136] A. P. Terent'ev and L. A. Solokhin, *Sintet. Kauchuk*, **1933** (5), 9; *Chem. Abs.*, 1934, **28**, 3385; *Brit. Chem. Abs.* **B**, 1934, 823.

[137] G. Egloff, *Nat. Pet. News*, 1935, **27** (47), 25; *Chem. Abs.*, 1936, **30**, 3212; *J. Inst. Pet. Tech.*, 1936, **22**, 52A. Discussion of the relative values of cracked and polymer gasoline has been given by: A. E. Dunstan, E. N. Hague and R. V. Wheeler, *Ind. Eng. Chem.*, 1934, **26**, 307; *J. Inst. Pet. Tech.*, 1934, **20**, 319A; *Brit. Chem. Abs.* **B**, 1934, 486. A. E. Dunstan, E. N. Hague and D. A. Howes, *Chimie et industrie*, 1935, **34**, 273; *Brit. Chem. Abs.* **B**, 1935, 934. A. E. Dunstan, *Trans. Faraday Soc.*, 1936, **32**, 227; *Chem. Abs.*, 1936, **30**, 2548; *Brit. Chem. Abs.* **B**, 1936, 306.

[138] The octane blending number is a number expressing the antiknock rating of a fuel when mixed in fixed proportions with a standard reference fuel. See Chapter 44 for a discussion of this topic.

[139] Reviews on the various processes have been given by: V. N. Ipatieff, B. B. Corson and G. Egloff, *Ind. Eng. Chem.*, 1935, **27**, 1077; *Brit. Chem. Abs.* **B**, 1935, 980. M. B. Cooke, H. R. Swanson and C. R. Wagner, *Refiner*, 1935, **14**, 497; *Oil Gas J.*, 1935, **34** (26) 57; *Nat. Pet. News.*, 1935, **27** (47), 33; *Chem. Abs.*, 1936, **30**, 1215, 2729; *J. Inst. Pet. Tech.*, 1936, **22**, 51A, 97A. P. C. Keith, Jr. and J. T. Ward, *Refiner*, 1936, **14**, 506; *Proc. Am. Petroleum Inst.*, Sect. III, 1935, **16**, 129; *J. Inst. Pet. Tech.*, 1936, **22**, 155A; *Chem. Abs.*, 1936, **30**, 3211. E. Ospina-Racines, *World Petroleum*, 1935, **6**, 616; *Chem. Abs.*, 1935, **29**, 8306. R. Heinze, *Öl u. Kohle*, 1936, **12**, 185; *Brit.*

Thermal Processes for Production of Polymer Gasoline. In the thermal process, either of two sets of conditions is usually practiced, low temperature-high pressure or high temperature-low pressure treatment.[140] Under the first set of conditions, below 800°F. (425°C.) and 500 to 3000 lbs. per sq. in. (35 to 200 atmospheres) pressure, straight chain hydrocarbons dominate in the product. The latter conditions [above 1000°F. (540°C.) and pressures less than 200 lbs. per sq. in. (about 15 atmospheres)] result in a liquid which is almost entirely aromatic in character.



Courtesy Pure Oil Co

FIG. 143.—Small Commercial Polymerization Unit.

Thermal polymer gasoline may be produced in any one of three methods, one-, two- or multi-stage, depending upon the composition of the feed gas. The one-stage process may be used with gases high in olefins, which can be polymerized directly, or simultaneous cracking and polymerization may take place, as in the so-called Unitary Process considered later in this chapter. In the case of gases with a high paraffin content, cracking is always necessary, so that a two-step method is employed in general. The multi-stage process is used only with gases having a large concentration of propene and butenes along with lower paraffins. The olefins are removed first by condensation, the remaining paraffins cracked in a second operation, and the resulting olefins are polymerized in a third step.

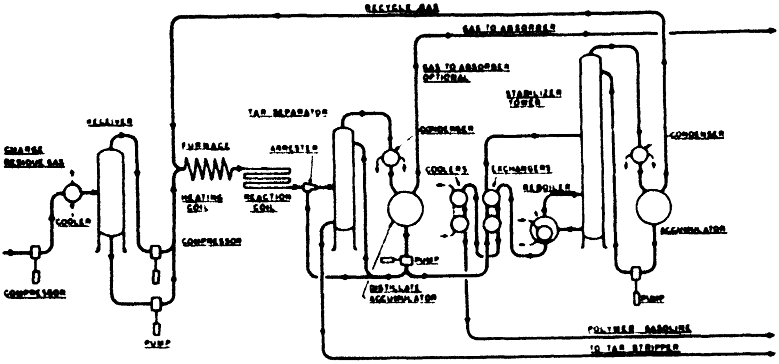
Chem. Abs. **B**, 1936, 435. C. O. Willson, *Oil Gas J.*, 1935, **33** (50), 16, 44; *J. Inst Pet. Tech.*, 1935, **21**, 307A; *Chem. Abs.*, 1935, **29**, 6019. *Petroleum Times*, 1936, **35**, 533; *J. Inst. Pet. Tech.*, 1936, **22**, 306A.

[140] Discussions of these processes are given by C. R. Wagner, *Ind. Eng. Chem.*, 1935, **27**, 933; *Chem. Abs.*, 1935, **29**, 6747; *J. Inst. Pet. Tech.*, 1935, **21**, 377A; *Brit. Chem. Abs.* **B**, 1935, 887. *Refiner*, 1936, **15**, 243; *J. Inst. Pet. Tech.*, 1936, **22**, 352A. M. B. Cooke, H. R. Swanson and C. R. Wagner, *Refiner*, 1935, **14**, 497; *Chem. Abs.*, 1936, **30**, 2729; *Oil Gas J.*, 1935, **34** (26), 57; *Nat. Pet. News*, 1935, **27** (47), 33; *J. Inst. Pet. Tech.*, 1936, **22**, 51A, 97A; *Chem. Abs.*, 1936, **30**, 1215. A. L. Foster, *Nat. Pet. News*, 1936, **28** (17), 43; *J. Inst. Pet. Tech.*, 1936, **22**, 305A.

Single-Stage Polymerization. Gases rich in olefins, such as those from vapor-phase cracking of hydrocarbon oils, may be polymerized directly to liquid fuels. Either high pressure-low temperature or high temperature-low pressure treatment may be employed. The yield of distillate is somewhat greater in the former case when operating on the same charging stock.[141]

Using the high pressure method, a flow sheet of which is given in Fig. 144, the gases are compressed to 600-800 lbs. per sq. in. pressure and heated to 900-1000°F. in a pipe-coil heater.[142] The gas is passed into a reaction chamber, ordinarily in the form of a coil which is cooled in order to absorb the exothermic heat of reaction[143] and is then chilled by injection of either cold gas or oil. Reaction is checked at about 60-70 per cent conversion. The product is then fractionated and the distillate stabilized, giving a yield of gasoline of 3.25 to 4.5 gal. per 1000 cu. ft.

The stock may also be charged in the liquid phase, which permits the elimination of low-molecular weight paraffins. The variation has several reported advantages, such as lower power costs due to removal of the inactive gases and a uniform control of polymerization reactions. Some tar-formation is traceable to the presence of ethylene since this olefin gives rise to such bodies at the operating temperatures required with propene-butene mixtures. However, the gasoline yield is only slightly reduced by the tar formation.



Courtesy Pure Oil Co.

FIG. 144.—Flow Sheet for High Pressure-Low Temperature Polymerization.

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[141] M. B. Cooke, H. R. Swanson and C. R. Wagner, *Nat. Pet. News*, 1935, **27** (47), 33; *J. Inst. Pet. Tech.*, 1936, **22**, 51A, 97A; *Chem. Abs.*, 1936, **30**, 1215.

[142] Plummer recommends the use of a preheating zone with low-content olefin gases (W. B. Plummer, U. S. P. 1,947,306, Feb. 13, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1934, **28**, 2367; *Brit. Chem. Abs.* **B**, 1934, 1048). The use of pressures up to 3500 lbs. per sq. in. is reported by M. P. Youcher, U. S. P. 1,976,469, Oct. 9, 1934, to Phillips Petroleum Co.; *Chem. Abs.*, 1934, **28**, 7517; *Brit. Chem. Abs.* **B**, 1935, 794. See also R. F. Ruthruff, Canadian P. 345,542, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 2338.

[143] The problem of absorbing the exothermic heat of polymerization has been discussed by C. R. Wagner (*Ind. Eng. Chem.*, 1935, **27**, 933; *Chem. Abs.*, 1935, **29**, 6747; *J. Inst. Pet. Tech.*, 1935, **21**, 377A; *Brit. Chem. Abs.* **B**, 1935, 887. Proposals for the utilization of this heat, such as for preheating feeds, are given by R. Ruthruff (U. S. P. 2,038,086, Apr. 21, 1936, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1936, **30**, 3834; *J. Inst. Pet. Tech.*, 1936, **22**, 264A). F. W. Sullivan, Jr., U. S. P. 2,031,987, Feb. 25, 1936, to Standard Oil Co. of Ind.; *J. Inst. Pet. Tech.*, 1936, **22**, 263A; *Chem. Abs.*, 1936, **30**, 2743. W. B. Plummer, U. S. P. 1,991,353, Feb. 12, 1935, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 2348; *Brit. Chem. Abs.* **B**, 1936, 87. R. E. Wilson, Canadian P. 345,537, 1934 and W. B. Plummer, Canadian P. 345,538, 1934, both to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 2340. W. B. Plummer and V. Voorhees, U. S. P. 1,991,354, Feb. 12, 1935, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 2348; *J. Inst. Pet. Tech.*, 1935, **21**, 174A; *Brit. Chem. Abs.* **B**, 1936, 87.

Table 138 summarizes typical data obtained in one-step polymerization processes under both high and low pressure treatment.[144]

TABLE 138.—*Effect of Operating Conditions on Polymerization Using Various Feed Stocks.*

	Residue from Gyro Vapor-Phase Cracking System	Liquid Fuel	Absorber Gas	Stabilizer Gas
Temperature, °F.	900-1000	900-1000	1275	1175
Pressure, lbs./sq. in.	600-800	600-800	60	55
Conversion, %	60-70	86.7	37.4	80
Recycle ratio	1.50	1.75	—	—
Charging stock (including recycle)				
Sp.Gr. (air = 1)	1.06	1.51	0.79	1.35
Unsaturates, mole %	47.2	49.4	39.4	79.6
Distillate made				
Gal./1000 cu. ft.	4.4	11.8	1.75	9.8
Percentage boiling up to 350°F.	84	75	76	68
Gravity of EP gasoline, °API	52.4	55.0	—	—
Octane number of gasoline, ASTM	78-80	76.0	102	86

Polymerization may be effected in the presence of an inert liquid medium, such as paraffin oil, at 300-500°C. under 20 to 50 atmospheres pressure.[145] Sullivan and Ruthruff[146] propose to employ a continuous system, using naphtha or gas oil as the solvent under 500 lbs. per sq. in. pressure and 650°F. Good yields of gasoline having a good antiknock rating are reported using this treatment.

The removal of hydrogen and methane from the feed gas may be accomplished in several ways. Ruthruff, Roberts and Carpenter[147] suggest the concentration of dilute olefin gases by scrubbing with liquid butane (under pressure) below 100°F. The absorbed gases are released from the butane solution by heating to 125-350°F. under 350-500 lbs. per sq. in. pressure, and subjected to polymerization. The liquid polymerization product may also be used for concentrating the feed gas. Plummer prefers to pass the liquid and gaseous products at a pressure of 500-3000 lbs. per sq. in. into a separator and introduce dilute olefinic gases through the liquid. The undissolved fixed gases are removed at the top of the separator and eliminated. The liquid and dissolved gases are withdrawn, the pressure released, and the concentrated olefinic gases introduced directly into the heating zone.[148] The gas mixture may also be subjected to pressures of about 1000 lbs. per sq. in. to liquefy hydrocarbons higher than methane. The uncondensed gases are thereby eliminated.[149]

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[144] M. B. Cooke, H. R. Swanson and C. R. Wagner, *loc. cit.*

[145] M. Hofsasz, U. S. P. 1,997,144, Apr. 9, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 3350; *J. Inst. Pet. Tech.*, 1935, **21**, 219A.

[146] F. W. Sullivan, Jr., and R. F. Ruthruff, Canadian P. 345,540, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 2340. See also G. Egloff, U. S. P. 1,988,112, Jan. 15, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 1620; *Brit. Chem. Abs.* **B**, 1935, 1077. M. P. Applebey and C. Cockram, British P. 415,792, 1934, to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1934, 952; *Chem. Abs.*, 1935, **29**, 918.

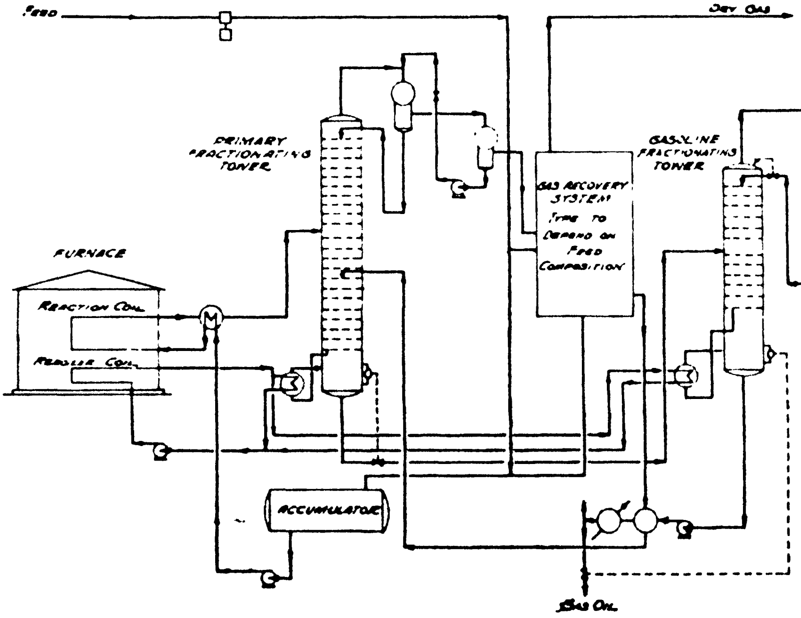
[147] R. F. Ruthruff, J. K. Roberts and M. T. Carpenter, U. S. P. 2,035,409, Mar. 24, 1936, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1936, **30**, 3222; *J. Inst. Pet. Tech.*, 1936, **22**, 211A. Canadian P. 356,810, 1936; *Chem. Abs.*, 1936, **30**, 3223. F. W. Sullivan, Jr., and R. F. Ruthruff, Canadian P. 340,080, 1934; *Chem. Abs.*, 1934, **28**, 3226 (both to Standard Oil Co.). See also C. R. Wagner and R. C. Osterstrom, British P. 451,788, 1936, to Pure Oil Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 450A; *Brit. Chem. Abs.* **B**, 1936, 969; *Chem. Abs.*, 1937, **31**, 533. Canadian P. 360,531, 1936; *Chem. Abs.*, 1936, **30**, 7836. French P. 786,207, 1935, to Pure Oil Co.; *Chem. Abs.*, 1936, **30**, 1228.

[148] W. B. Plummer, U. S. P. 1,940,227, Dec. 19, 1933, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1934, **28**, 1522; *Brit. Chem. Abs.* **B**, 1934, 870; *J. Inst. Pet. Tech.*, 1934, **20**, 112A. See also K. R. Finsterbusch, British P. 428,475, 1935; *Chem. Abs.*, 1935, **29**, 7063; *Brit. Chem. Abs.* **B**, 1935, 759.

[149] R. E. Wilson, Canadian P. 345,541, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 2340.

Plummer suggests the use of two complementary treatments. Rich olefins are subjected to a relatively low temperature (370-510°C.) while lean gases are treated at higher temperatures (510-675°C.), in separate units, at pressures of 500 to 3000 lbs. per sq. in. The liquid products are separated and from the first system a lean olefinic gas is obtained, while the second gives a gas rich in unsaturates. These gases are then recycled to the respective high and low temperature systems.[150]

The Unitary Process. One method of thermal polymerization, the so-called Unitary Process, has been studied by Keith and Ward.[151] According to these investigators, thermal polymerization and cracking occur simultaneously in this process, and under the proper conditions, the specific rates of reaction are controllable and direct conjugation of saturates with unsaturates can be brought about.


Feed
Dry Gas
Primary Fractionating Tower
Furnace
Reaction Coil
Reboiler Coil
Gas Recovery System Type to Depend on Feed Composition
Gasoline Fractionating Tower
Gasoline
Accumulator
Gas Oil

Courtesy Oil and Gas Journal

FIG. 145.—Flow Diagram of Unitary Process. (J. T. Ward)

The charging stocks may vary from natural or refinery gases to the complex mixtures found in stabilizer reflux or absorber oil distillates. Separation of the paraffinic and olefinic hydrocarbons is normally not required. The yield and nature of the product will vary according to the composition of the feed stock, a highly unsaturated gas (70 per cent) giving a liquid lower in specific gravity, lower in paraffins and higher in aromatics than a low olefin content feed gas (one containing only 15 to 35 per cent unsaturates). A yield of 14 gal. of liquid with a blending value[152] of 80 to 120 is said to be obtained per 1000 cu. ft. of natural or refinery gas. The operating conditions are temperatures of 480 to 580°C. (900-1075°F.) and 800 to 2200 lbs. pressure. A flow sheet of this process is given in Fig. 145.

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[150] W. B. Plummer, U. S. P. 1,941,577, Jan. 2, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1934, **28**, 1714; *J. Inst. Pet. Tech.*, 1934, **20**, 192A; Canadian P. 341,531, 1934; *Chem. Abs.*, 1934, **28**, 4900.

[151] P. C. Keith, Jr. and J. T. Ward, *Refiner*, 1935, **14**, 506; *Proc. Am. Petroleum Inst.*, Sect. III, 1935, **16**, 129; *Chem. Abs.*, 1936, **30**, 3211. *Nat. Pet. News*, 1935, **27** (47), 52; *Chem. Abs.*, 1936, **30**, 3212; *J. Inst. Pet. Tech.*, 1936, **22**, 155A. *Chem. and Ind.*, **1936**, 532; *Brit. Chem. Abs.* **B**, 1936, 915. J. T. Ward, *Oil Gas J.*, 1936, **35**, 137. See also *Refiner*, 1935, **14**, 480; *Oil Gas J.*, 1935, **34** (20), 26; *J. Inst. Pet. Tech.*, 1935, **21**, 451A, 453A.

The data on four typical pilot-plant operations are given in Table 139.

TABLE 139.—*Simultaneous Cracking and Polymerization (Unitary Process) Using Recycling Operation.*

Pressure, lbs./sq. in.	800	1200	1200	1200
Temperature, °F.	1000	1000	1100	1030
Net Yield, % by weight	67.9	69.0	69.6	64.5
Weight, % of saturates in feed (net)	57.0	54.0	60.7	59.9
Weight, % of unsaturates in feed (net)	43.0	46.0	39.3	40.1
Net yield as % of unsaturates in fresh feed	158	150	177	161
Gallons of liquid per 1000 cu. ft. net gaseous feed	12.78	13.10	14.40	13.5
Gross feed, volume %				
C_2H_4	3.4	1.9	2.4	2.0
C_2H_6	12.2	6.8	9.6	6.5
C_3H_6	29.6	30.5	21.3	21.0
C_3H_8	46.3	49.8	38.8	29.6
C_4H_8	4.3	4.8	11.0	13.6
C_4H_{10}	4.2	6.2	16.9	17.3
Blending value of 400°F. EP. distillate, 50% in "A" reference fuel, octane number, C.F.R.M.[152a]	92	90	83	88

Two-Stage Process. Operations, involving combination of pyrolysis and polymerization steps, are described by Cooke, Swanson and Wagner.[153] They point out that gases from cracking stills of the so-called liquid-vapor phase type are particularly applicable as charging stocks. Using the high-temperature-low pressure polymerization treatment, the resulting gasoline is reported to contain 80 to 85 per cent aromatics and to have a knock rating of 100 octane number. Burk recommends cracking the gas at 1600-2100°F. (870-1150°C.), cooling to 1100°F. and then polymerizing at 1350-1750°F.[154]

Table 140 gives data obtained in a high-temperature operation using natural gas as the charging stock.

Frolich and Wiezevich[155] obtained the highest yield of liquids from propane by using a two-stage process with intermediate removal of hydrogen. They noted that in the pressure treatment of cracked gas there is a pronounced tendency for the hydrogen present to saturate ethylene and propene, thus decreasing liquid formation. Table 141 gives their results using a simultaneous cracking-polymerization operation, a two-step process, and a special method in which the hydrogen was removed previous to the polymerization step by heating with copper oxide for 2 to 5 seconds at 300-350°C.

Copper oxide treatment removed 90 per cent of the hydrogen, with only a small loss of olefins, and the high pressure method could be used to advantage.

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[152] See Chapter 44 for a discussion of blending values of fuels.

[152a] This is the Cooperative Fuel Research Method. See Chapter 44, this text.

[153] M. B. Cooke, H. R. Swanson and C. R. Wagner, *Nat. Pet. News*, 1935, **27** (47), 33; *J. Inst. Pet. Tech.*, 1936, **22**, 51A, 97A; *Chem. Abs.*, 1936, **30**, 1215.

[154] R. E. Burk, U. S. P. 2,033,878, Mar. 10, 1936, to Standard Oil Co. of Ohio; *J. Inst. Pet. Tech.*, 1936, **22**, 211A; *Chem. Abs.*, 1936, **30**, 3216. See also H. M. Smith and H. T. Rall, U. S. P. 1,967,269, July 24, 1934; *J. Inst. Pet. Tech.*, 1934, **20**, 535A; *Chem. Abs.*, 1934, **28**, 5975. J. H. Boyd, Jr., U. S. P. 2,042,452, June 2, 1936, to Atlantic Refining Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 401A; *Chem. Abs.*, 1936, **30**, 5023.

[155] P. K. Frolich and P. J. Wiezevich, *Ind. Eng. Chem.*, 1935, **27**, 1055; *Chem. Abs.*, 1935, **29**, 7624; *Brit. Chem. Abs.* **B**, 1935, 980.

TABLE 140.—*Polymer Gasoline from Natural Gas, Using a Two-Stage Process.*

Charge Gas:	
Specific gravity (air = 1)	0.815
Composition: volume %	
CH_4	70.5
C_2H_6	12.7
C_3H_8	10.3
C_4H_{10} and heavier	6.5
Pyrolysis Gas:	
Specific gravity (air = 1)	0.645
Composition:	
H_2	11.5
CH_4	62.5
C_2H_4	15.7
C_2H_6	5.1
C_3H_6	2.5
C_3H_8	1.2
C_4 and heavier	1.5
Liquid Made:	
Pyrolysis step, gal./1000 cu. ft. of charge	0.42
Polymerization	2.38
Total	2.80
Percentage boiling up to 350°F.	75
Octane number, ASTM	104

Frolich[156] has also suggested the use of metallic copper as a catalyst for oxidizing the hydrogen to water. Thus, a typical cracked propane gas (39 per cent olefins, 31 per cent lower paraffins and 30 per cent hydrogen) was mixed with 15 per cent of oxygen and passed over copper shot at 400°C. The exit gas from this treatment contained substantially no free hydrogen. The material was dried, compressed to 600 lbs. per sq. in. and heated at 525°C. for 30 minutes, giving a yield of 4.56 gallons of liquid per 1000 cu. ft. of propane originally charged.

TABLE 141.—*Cracking and Polymerization of Propane.*

	Polymerization Conditions		Gallons per 1000 cu. ft.	
Method	Temp. °C.	Pressure lbs./sq. in.	Best Yield	Light Oil
Simultaneous	880	Atmos.	4.4	1.52
Two-Step	650	700	1.95	1.29
Two-Step with intermediate hydrogen removal	400	2500	7.75	5.73
	400	600	—	4.56

White and Frolich[157] have reported that nickel, tin and iron and their oxides could also be substituted as catalysts in place of copper. When the above mentioned metals are employed, temperatures of 300 to 450°C. are said to be most effective. However, with the metallic oxides, much lower temperatures (ordinarily 200-350°C.) may be used. The presence of sulphur is objectionable, in that it poisons the catalyst. It is therefore customary to remove this element by scrubbing the gases with sodium hydroxide solution. White and Frolich found only small proportions (less than 1 per cent) of carbon monoxide and carbon dioxide in the hydrogen-free gas, showing that in the presence of the above catalysts, the oxygen combined with hydrogen in preference to carbon or hydrocarbons.

Another method of hydrogen removal is to add carbon monoxide prior to the polymerization step. Frolich[158] found that in the presence of a catalyst, consisting of nickel mixed with aluminum oxide, reaction between the carbon monoxide and hydrogen takes place at 200-350°C. under 100 atmospheres pressure. Frolich has also suggested using carbon dioxide in place of carbon monoxide. Nickel oxide, in finely divided form, likewise has a catalytic effect, especially if small amounts of thorium, chromium, vanadium, molybdenum, magnesium or boron oxides are added. According to Wiezevich and Whiteley,[159] the addition of small amounts of air or oxygen to the olefinic gases lowers the temperature and pressure required for polymerization. The oxygen is only necessary to initiate the polymerization reactions, and after once started, the condensation is said to run smoothly without further introduction of oxygen. These investigators prefer to heat the olefins to 200-400°C. at pressures of 10 to 200 atmospheres and then add 0.01 to 0.04 moles of oxygen. The reaction time is ordinarily in the magnitude of 8 to 10 hours. The product obtained by this treatment contains cycloparaffins, aromatics, higher olefins and some oxygenated compounds. Large proportions of oxygen, however, are said to have an adverse effect, causing the formation of large amounts of carbon, water and fixed gases.

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[156] P. K. Frolich, U. S. P. 1,869.681, Aug. 2, 1932, to Standard Oil Development Co.; *Chem. Abs.*, 1932, 26, 5412; *Brit. Chem. Abs.* B, 1933, 536.

[157] A. White and P. K. Frolich, U. S. P. 1,911,780, May 30, 1933, to Standard Oil Development Co.; *Chem. Abs.*, 1933, 27, 4039; *Brit. Chem. Abs.* B, 1934, 283.

[158] P. K. Frolich, U. S. P. 2,002,534, May 28, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1935, 29, 4373; *J. Inst. Pet. Tech.*, 1935, 21, 266A.

Guyer[160] also advocates a two-stage treatment. Thus, olefinic gases are polymerized at pressures of about 500 lbs. per sq. in., and at the same time, in a separate unit, a paraffinic stock (consisting mostly of propane, butane and pentane hydrocarbons) is cracked at high pressures (about 1000 lbs. per sq. in.) and the products of the two stages combined and separated into liquid and gaseous phases. The gases are fractionated into a light portion (below butane), which is discarded, and a butane fraction, which is returned to the pyrolytic unit and mixed with the fresh paraffinic charge.

Three-Stage Process (Multi-Stage). A typical charging stock for this type of operation consists of the stabilizer overhead containing about 30 per cent unsaturates. By polymerizing as the initial step, there is a distinct advantage in that the propene and butene can be converted to gasoline under the most favorable conditions. Fig. 146 shows the various phases of operation.

In the primary polymerization step, the charge is heated to the proper temperature and enters the reaction coil which is designed to give the desired time-temperature effect. Cooling means must be provided to keep the temperature within the proper limits. Immediately after leaving the coil, the reaction products are chilled to stop any further reaction. The total overhead passes to a cooler and accumulator where the chilling medium, polymerized distillate and a portion of the gaseous constituents are condensed. The remaining vapors and gases from this stage are passed directly into the pyrolysis unit and subjected to treatment analogous to the two-stage methods previously mentioned.[161]

Fractional polymerization may be effected by special processing. Ruthruff suggests treatment in at least three stages at progressively lower pressures to bring about this purpose. After the first polymerization stage, the fixed gases, such as methane and hydrogen, are separated and eliminated from the system. The subsequent steps are regulated, as regards temperature and pressure, so as to produce maximum yields of liquids. Concentrated olefinic gases are returned to the cycle, but more dilute gases are treated in distinct systems under the most appropriate conditions.[161a] The most favorable conditions reported by Ruthruff are given in Table 142.

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[159] P. J. Wiezevich and J. M. Whiteley, U. S. P. 1,981,819, Nov. 20, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 474; *Brit. Chem. Abs.* B, 1935, 881.

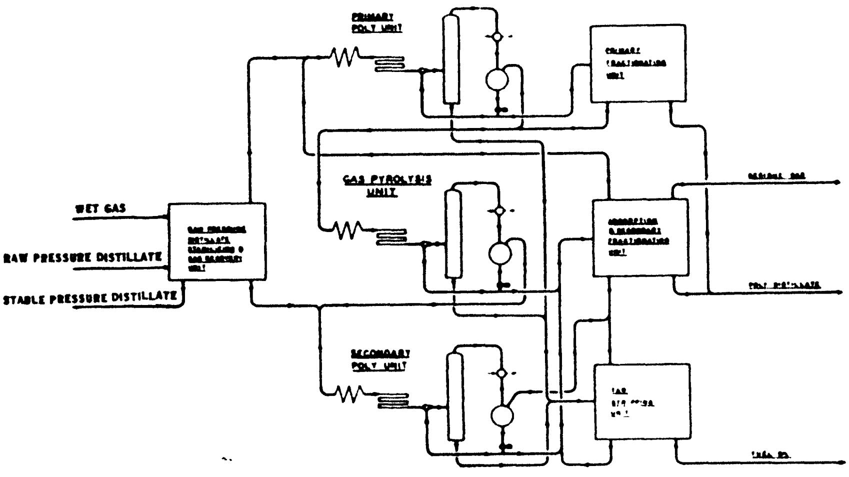
[160] J. A. Guyer, U. S. P. 2,054,599, Sep. 15, 1936, to Phillips Petroleum Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 544A; *Chem. Abs.*, 1936, **30**, 7836.

[161] M. B. Cooke, H. R. Swanson and C. R. Wagner, *Nat. Pet. News*, 1935, **27** (47), 33; *J. Inst. Pet. Tech.*, 1936, **22**, 51A, 97A; *Chem. Abs.*, 1936, **30**, 1215.

TABLE 142.—*Conditions for Multi-Stage Polymerization*

Olefin Content %	Pressure kg./sq.cm.	Temperature °C.
Over 50	35-210	370-510
20-50	35-210	510-675
Less than 20	0-14	705-955

Catalytic Process for Production of Polymer Gasoline. This process may be defined as a method whereby cracked or dehydrogenated hydrocarbon gases are subjected to mild heat and pressure while flowing through a solid catalyst.[162] Using phosphoric acid as catalyst, relatively few types of polymers are produced so that the resulting liquid is of quite constant composition.



Courtesy Pure Oil Co.

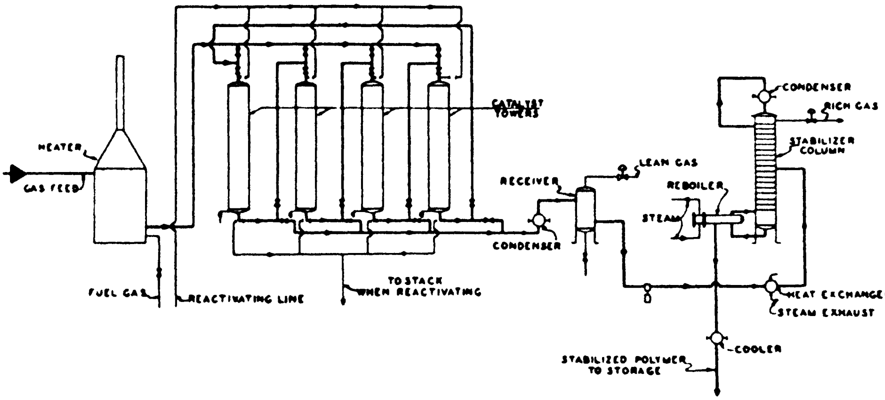
FIG. 146.—Sketch of Three-stage Process of Polymerization.

The "solid" phosphoric acid catalyst,[163] consisting of phosphoric acid supported on an inert carrier, is generally used. The catalyst is prepared by mixing phosphoric acid (18 parts of 75 to 100 per cent phosphoric acid) with the carrier (7 parts) and calcining the resulting magma at 180-300°C. for 20 to 60 hours to remove most of the water. Supporting media which may be used are siliceous materials (such as kieselguhr, fuller's earth and bentonite), zinc or aluminum oxide and magnesium or calcium chloride. In addition, organic substances, for example, cellulose, starch, glue, gelatin and tar, may be incorporated to furnish a residue of carbon after calcining. In certain cases, to prevent the loss of water from the catalyst during operation, steam may be admixed with the olefinic gases.[104] Temperatures of 100 to 250°C. are advocated for this process. The catalyst is described as a hard non-corrosive solid whose action is not poisoned by carbon monoxide, hydrogen sulphide, mercaptans, or other constituents of refinery gases. Nevertheless, after protracted use, it becomes inactivated by contamination with high-molecular weight material. However, reactivity can be restored by mild oxidation (such as with air or oxygen) without removing the catalyst from its position in the contact towers.[105]

[161a] R. F. Ruthruff, U. S. P. 2,017,325, Oct. 15, 1935, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 7999; *Brit. Chem. Abs.* **B**, 1936, 629. French P. 759,718, 1934; *Chem. Abs.*, 1934, **28**, 3415.

[162] G. Egloff, *Oil Gas J.*, 1936, **34** (44), 140; 1936, **35** (22), 58; *Chem. Abs.*, 1936, **30**, 5401, 8588. *Petroleum Times*, 1936, **36**, 527; *J. Inst. Pet. Tech.*, 1936, **22**, 546A. Discussions on the catalytic polymerization of olefins to gasoline have also been given by: V. N. Ipatieff and G. Egloff, *Oil Gas J.*, 1935, **33** (52), 31; *Petroleum Eng.*, 1935, **6** (10), 29; *Petroleum Z.*, 1935, **31** (29), 1; *Chem. Abs.*, 1935, **29**, 6410; *J. Inst. Pet. Tech.*, 1935, **21**, 307A; *Brit. Chem. Abs.* **B**, 1935, 757. R. Fussteig, *Petroleum Z.*, 1936, **32** (29), 6; *J. Inst. Pet. Tech.*, 1936, **22**, 401A; *Chem. Abs.*, 1936, **30**, 7828. C. R. Wagner, *Nat. Pet. News*, 1936, **28** (18), 22; *J. Inst. Pet. Tech.*, 1936, **22**, 352A. J. S. Cary, *Gas*, 1936, **12** (11), 20; *Chem. Abs.*, 1937, **31**, 523. A. L. Foster, *Nat. Pet. News*, 1935, **27** (17), 35; 1935, **27** (47), 22; *J. Inst. Pet. Tech.*, 1935, **21**, 258A; 1936, **22**, 52A. Also *Nat. Pet. News*, 1935, **27** (18), 24D; *J. Inst. Pet. Tech.*, 1935, **21**, 258A.

[163] V. N. Ipatieff, U. S. P. 1,993,512, Mar. 5, 1935; 1,993,513, Mar. 5, 1935; 2,018,065, Oct. 22, 1935; 2,020,649, Nov. 12, 1935; *Chem. Abs.*, 1935, **29**, 2546; 1936, **30**, 281, 484; *Brit. Chem. Abs.* **B**, 1936, 777, 1096. U. S. P. 2,057,433, Oct. 13, 1936; *J. Inst. Pet. Tech.*, 1937, **23**, 20A; *Chem. Abs.*, 1936, **30**, 8598. British P. 437,188, 1935; *Chem. Abs.*, 1936, **30**, 2361; *Brit. Chem. Abs.* **B**, 1936, 8; *J. Inst. Pet. Tech.*, 1936, **22**, 23A. French P. 797,584, 1936; *Chem. Abs.*, 1936, **30**, 7582. All to Universal Oil Products Co.



Courtesy Oil and Gas Journal

FIG. 147.—Flow Sheet of Polymerization Process Employing Solid Phosphoric Acid Catalyst. (G. Egloff)

A flow sheet of this process is given in Fig. 147. The feed, which may be gases from gasoline receivers, stabilizer tops or stabilizer reflux of cracking installations, cracking units or catalytic dehydrogenation units, is led to a pipe coil heater, which is maintained at 400°F. and a pressure of 200 lbs. per sq. in. The gas flows from the heater into a series of catalyst chambers or towers. A temperature rise of about 100°F. occurs in the catalyst bed due to the exothermic polymerization reaction. The polymer vapors pass through a cooling coil into a receiver, where the liquids are separated and stabilized.

Olefins are converted to liquid polymers, substantially of the monolefin type, by this treatment. Residual gaseous paraffins may be catalytically dehydrogenated and recycled over the catalyst as above. If the concentration of hydrogen sulphide in the feed gas is high, mercaptans will be formed during the polymerization, so the sulphides are generally removed prior to catalysis.[106] Over 75 per cent by weight of the original gaseous hydrocarbons can be converted to a gasoline of 81 to 83 octane number. The volume yield, based on a 50-50 propane-butane mixture, is over 19 gal. per 1000 cu. ft.[167]

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[104] V. N. Ipatieff, U. S. P. 2,018,066, Oct. 22, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 109; *J. Inst. Pet. Tech.*, 1935, **21**, 458A.

[105] V. N. Ipatieff and G. Egloff, *loc. cit.* V. N. Ipatieff, B. B. Corson and G. Egloff, *Ind. Eng. Chem.*, 1935, **27**, 1077; *J. Inst. Pet. Tech.*, 1935, **21**, 413A; *Brit. Chem. Abs.* B, 1935, 980.

[106] See Chapter 19 for a discussion of various methods for separation of mercaptans from hydrocarbons. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

Ipatieff, Corson and Egloff have studied the effect of variations in temperature, pressure, rate of flow and the nature of the reacting gases.[168] The latter were from four sources, receiver gas, stabilizer reflux, stabilizer gas and commercial ethylene. The receiver gas was obtained in the liquid-vapor phase cracking (500°C., 200 lbs. pressure) of mixed Mid-Continent and West Texas topped crude. The stabilizer reflux was derived from stabilization of cracked gasoline from the above cracking treatment. The stabilizer gas came from stabilization of a gasoline from vapor-phase cracking of gas oil at 550°C. and atmospheric pressure. Results of various runs, along with comparative tests made on commercial ethylene (98 per cent ethylene and 2 per cent ethane) with the same apparatus are given in Table 143. From the results, it will be noted that the highest yield of total liquids was obtained from ethylene treated at 324°C. and 520 lbs. per sq. in. pressure with a gas velocity of 2.5 cu. ft. per hour per pound of catalyst. In this case, however, the proportion of gasoline in the product was less than 50 per cent. Shorter contact periods at the same temperature and pressure decreased the total quantity of liquids produced but increased the gasoline content to about 65 per cent. The highest percentage yield of gasoline was obtained using the most dilute olefin gas (receiver gas), 93 per cent of the total liquid boiling in the gasoline range (below 400°F.). The maximum yield of gasoline, 7.1 gal. per 1000 cu. ft. of gas, resulted from the treatment of stabilizer reflux at 232°C. and 100 lbs. per sq. in. pressure using the slowest gas velocity, 0.3 cu. ft. per hr. per lb. catalyst.

TABLE 143.—*Polymerization of Cracked Gases and Ethylene Using a Solid Phosphoric Acid Catalyst.*

	Receiver Gas			Stabilizer Gas			Stabilizer Reflux			Commercial Ethylene		
Conditions:												
Duration of Test, Hours	120	120	120	72	72	72	120	72	72	228	194	264
Pressure, lbs./sq.in.	200	200	200	100	100	100	100	100	100	520	520	520
Temperature, °C.	204	232	232	204	204	204	232	232	232	296	324	324
Inlet Gas Rate, cu.ft./hr./lb. Catalyst	2.1	1.3	0.5	4.9	3.4	2.1	1.7	0.9	0.3	1.5	2.5	3.4
Olefin Content of Reacting Gas:												
Propene and Butenes	17.3	18.6	16.8	37.5	37.5	37.5	43.9	42.6	42.7	..	..	—
Ethylene	6.6	7.2	7.0	—	—	—	20.2	21.6	21.2	98	98	98
Extent of Polymerization, %:												
Propene and Butenes	64	79	95	72	81	89	84	94	96			
Ethylene	13	16	31	—	—	—	9	25	32	73	72	65
Yield of Liquid Product, Gallons per 1000 cu. ft.:												
Crude Polymer	2.9	3.8	4.0	6.0	6.9	7.2	7.6	8.5	8.4	8.0	9.9	7.1
Gasoline	2.7	3.5	3.7	5.4	6.2	6.5	6.3	7.1	7.0	4.7	4.7	4.6
Characteristics of Gasoline:												
Initial Boiling Point	134			150			142			106		
End Point, °F.	401			389			414			398		
Sp. Gr. at 60°F.	0.732			0.728			0.738			0.711		
Octane Number (CFR Motor Method)	82			82			82			82		
Sulphur, %	0.4			0.18			0.04			—		
Gum, mg./100 cc. (Copper Dish)	5			4			72			10		

In addition to the solid phosphoric acid catalyst, Ipatieff has also suggested the use of aqueous phosphoric or phosphorous acids.[169] In this instance the olefinic gases are bubbled through the solution at 60° to 200°C. Polymerization of lower olefins by means of phosphoric acid may also be carried out in the presence of extraneous liquid olefins.[170] The reaction may also be brought about with low boiling liquid hydrocarbons by suspending phosphorus pentoxide in a solvent to which has been added a peptizing agent[171] (an organic compound containing a hydroxyl group, e.g., cresol). By thermally cracking natural and straight-run gasoline and polymerizing the olefins by means of phosphoric acid treatment, the antiknock properties of the fuel are said to be increased.[172]

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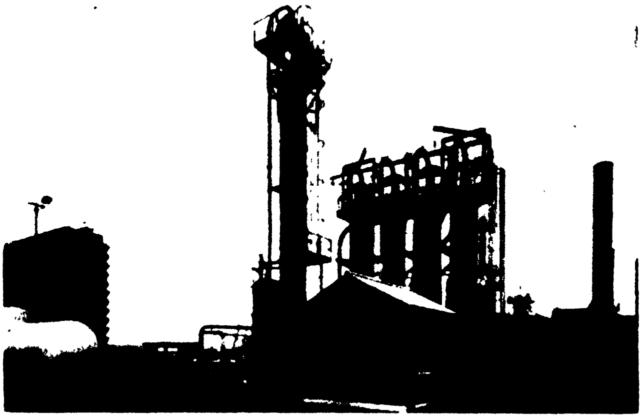
[167] G. Egloff, *Oil Gas J.*, 1936, **34** (44), 140; *Chem. Abs.*, 1936, **30**, 5401.

[168] V. N. Ipatieff, B. B. Corson and G. Egloff, *loc. cit.* V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, 1936, **28**, 860; *Chem. Abs.*, 1936, **30**, 5764; *J. Inst. Pet. Tech.*, 1936, **22**, 350A.

[169] V. N. Ipatieff, U. S. P. 1,960,631, May 29, 1934, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1935, 295; *J. Inst. Pet. Tech.*, 1934, **20**, 458A. Canadian P. 353,253, 1935; *Chem. Abs.*, 1935, **29**, 8316.

Other Catalysts for Producing Polymer Gasoline. Various metals have been proposed as catalysts. For example, olefins may be polymerized at 400-900°C. by conducting them over metal surfaces, coated or alloyed with tin, zinc, aluminum or chromium.[173] The use of platinum and palladium at 177-371°C. and 40 to 140 atmospheres pressure[174] and powdered zinc or iron oxide at low temperatures and high pressures[175] has been outlined. Burk proposes to employ the vapors of zinc or cadmium, or high-boiling salts, such as lead chloride, at temperatures above 700°C.[176] Volatile metallic halides, such as the chlorides of aluminum, nickel, iron, or titanium, or aluminum bromide, at 175-375°C. and 600 to 1500 lbs. per sq. in. pressure are recommended by Wagner.[177] An aqueous solution of hydrochloric acid in conjunction with brass is also said to exert a polymerizing action.[178]



Courtesy Industrial and Engineering Chemistry

FIG. 148.—View of Catalytic Polymerization Unit. Capacity 3 million cu. ft. of gas per day. (V. N. Ipatieff, B. B. Corson and G. Egloff)

Porous materials, having a large surface-volume ratio, are also applicable as contact agents. For example, Towne[179] employs adsorptive clays for this purpose. Gases containing 50 per cent of olefins (obtained from cracking of natural and refinery gases) are converted at 450° to 500°C. and pressures in excess of 1500 lbs. per sq. in. into straight chain polymers. Mixtures of acid-treated montmorillonite clay (200 mesh or finer) with 5-25 per cent of diatomaceous earth to reduce the resistance of the clay to the flow of vapors and gases have been described.[180] Wagner advocates the use of agents such as bentonite, silica gel, or activated charcoal. He attributes the catalytic properties of these substances to their selective adsorptive powers, which give local high concentrations of the unsaturated gases and thus promote specific polymerization reactions.[181]

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[170] V. N. Ipatieff and V. Komarewsky, U. S. P. 2,051,859, Aug. 25, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 6757; *J. Inst. Pet. Tech.*, 1936, **22**, 451A.

[171] B. W. Malishev, U. S. P. 2,055,415, Sept. 22, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 7586; *J. Inst. Pet. Tech.*, 1936, **22**, 544A.

[172] G. Egloff, U. S. P. 1,983,693, Dec. 11, 1934, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 920; *Brit. Chem. Abs.* B, 1935, 1128; *J. Inst. Pet. Tech.*, 1935, **21**, 97A.

[173] F. Winkler and H. Häuber, German P. 593,248, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 3078.

[174] C. R. Wagner, U. S. P. 1,913,691, June 13, 1933, to Pure Oil Co.; *Brit. Chem. Abs.* B, 1934, 183; *Chem. Abs.*, 1933, **27**, 4390.

[175] P. Kaisler and F. Stockert, French P. 765,333, 1934; *Chem. Abs.*, 1934, **28**, 6894.

[176] R. E. Burk, U. S. P. 1,991,593, Feb. 19, 1935, to Standard Oil Co. of Ohio; *Brit. Chem. Abs.* B, 1936, 87; *Chem. Abs.*, 1935, **29**, 2350.

[177] C. R. Wagner, U. S. P. 1,934,896, Nov. 14, 1933, to Pure Oil Co.; *Chem. Abs.*, 1934, **28**, 631; *Brit. Chem. Abs.* B, 1934, 790.

[178] J. C. Morrell, U. S. P. 2,055,875, Sept. 29, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 8597; *J. Inst. Pet. Tech.*, 1936, **22**, 545A.

REFINING OF CRACKED GASOLINE

An interesting and important phase of olefin polymerization is in the refining of cracked petroleum distillates. One of the problems in the storage and sale of cracked gasolines is the maintenance of its desirable properties, particularly in respect to color stability, antiknock properties and gum formation. The latter is associated with oxidation phenomena, especially in the case of diolefins containing conjugated bonds.[182] These hydrocarbons are markedly more unstable than monoolefins. Therefore, removal of such objectionable compounds is of considerable interest.[183]

The effect of high pressure, even up to 9000 atmospheres, on cracked gasoline has been discussed by Starkweather.[184] Treatment under these high pressures at 60°C. for 48 hours gave no indication of resinous products. However, 10 per cent of the low boiling constituents, mainly diolefins, were converted to higher boiling compounds.

Refining involving chemical treatment is usually necessary to effect removal of gum-forming constituents. Such operations may be carried out in the vapor phase, as for instance in the Gray and Lachman processes, or in the liquid phase, as exemplified by the method developed by Day (see below) and by the use of sulphuric acid.

Gray Process. Gray[185] proposed treatment of the hydrocarbon vapors with a solid adsorptive catalyst, such as fuller's earth. It was noted that, by this processing, diolefins and other unstable substances were polymerized to viscous oils or resinous solids while monolefins were practically unaffected. The volume loss was reported as less than 1 per cent. The procedure is said to be applicable also to gaseous olefins resulting in their polymerization to products boiling within the gasoline range.[186] In discussing the Gray process, Steininger[187] points out that a study of the factors influencing the treated material showed that rate of treatment, clay usage rate, the type of stock employed and the conditions of cracking affect the characteristics of the final product. Generally 5000 to 6000 barrels of refined distillate are obtained per ton of clay. Increased yields can be effected by use of higher pressures and temperatures with increased contact time.

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[179] C. C. Towne, Canadian P. 342,496, 1934, to Texaco Development Corp.; *Chem. Abs*, 1934, **28**, 5831. See also T. T. Gray, U. S. P. 2,034,575, Mar. 17, 1935, to Gray Process Co.; *Chem. Abs.*, 1936, **30**, 3206; *J. Inst. Pet. Tech*, 1936, **22**, 211A.

[180] M. Halpern, W. B. Logan, R. E. Manley and W. Ullrich, U. S. P. 2,030,030, Feb. 4, 1936; to Texas Co.; *Chem. Abs.*, 1936, **30**, 1991; *J. Inst. Pet. Tech.*, 1936, **22**, 151A.

[181] C. R. Wagner, U. S. P. 1,938,945, Dec. 12, 1933, to Pure Oil Co.; *Chem. Abs.*, 1934, **28**, 1523; *Brit. Chem. Abs.* **B**, 1934, 869; *J. Inst. Pet. Tech.*, 1934, **20**, 112A.

[182] See Chapter 40. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[183] J. C. Morrell and G. Egloff, *Nat. Pet. News*, 1936, **28** (12), 33, (13), 24G, (15), 24L, (16), 37; *Chem. Abs.*, 1936, **30**, 4656; *J. Inst. Pet. Tech.*, 1936, **22**, 265A, 309A. Reviews of refining are also given by C. G. Verver and R. N. J. Saal, *J. Inst. Pet. Tech.*, 1934, **20**, 367; *Chem. Abs.*, 1934, **28**, 4889; *J. Inst. Pet. Tech.*, 1934, **20**, 414A; and E. V. Bart, V. N. Erikh and Y. G. Gervart, *Materials on Cracking and Chem. Treatment of Products Obtained, Goskhimtekhizdat*, 1933, 1, 138; *Chem. Abs.*, 1935, **29**, 2718; *Brit. Chem. Abs.* **B**, 1935, 1030.

[184] H. W. Starkweather, *J.A.C.S.*, 1934, **56**, 1870; *Chem. Abs.*, 1934, **28**, 6700; *Brit. Chem. Abs.* **A**, 1934, 1198.

[185] T. T. Gray, U. S. P. 1,340,889, May 25, 1920, to Gray Process Corp.; *J.S.C.I.*, 1920, **39**, 651A; *Chem. Abs.*, 1920, **14**, 2261. T. T. Gray and M. R. Mandelbaum, *Ind. Eng. Chem.*, 1924, **16**, 913; *Chem. Abs.*, 1924, **18**, 3473; *J.S.C.I.*, 1924, **43**, B857. Several modifications of the original procedure have been suggested. These include the use of beds of catalyst, regulation of vapor flow to remove polymers, employment of condensed vapors and steam to cleanse catalysts, utilization of the heat evolved and various designs of apparatus employed. See T. T. Gray, U. S. P. 1,759,812, 1,759,813, 1,759,814, May 20, 1930; *Chem. Abs.*, 1930, **24**, 3636; *Brit. Chem. Abs.* **B**, 1931, 193. British P. 222,481, 1924 and 249,871, 1925; *Brit. Chem.* Abs. **B**, 1926, 230; 1927, 290; *Chem. Abs.*, 1925, **19**, 1049; 1927, **21**, 1007. U. S. P. 1,853,972, Apr. 12, 1932; *Brit. Chem. Abs.* **B**, 1933, 138; *Chem. Abs.*, 1932, **26**, 3371. U. S. P. 1,952,855, Mar. 27, 1934; *Chem. Abs.*, 1934, **28**, 3884; *J. Inst. Pet. Tech.*, 1934, **20**, 376A. E. A. Dickinson, U. S. P. 1,853,671, Apr. 12, 1932; *Brit. Chem. Abs.* **B**, 1933, 138; *Chem. Abs.*, 1932, **26**, 3370. P. S. Nisson, U. S. P. 1,948,126, Feb. 20, 1934; *J. Inst. Pet. Tech.*, 1934, **20**, 320A; *Chem. Abs.*, 1934, **28**, 2888. All patents to Gray Process Corp. *Cf.* A. G. Connolly, U. S. P. 1,934,967 and 1,934,968, Nov. 14, 1933, to Universal Oil Products Co.; *Chem. Abs.*, 1934, **28**, 628; *J. Inst. Pet. Tech.*, 1934, **20**, 40A. W. M. Stratford, U. S. P. 1,962,752, June 12, 1934,

A description of the Gray process has been given also by Mandelbaum.[188] He states that the best results are secured when operating near the dew point, so that the gasoline is in the vapor phase, but the polymers remain liquid. With increased pressure, efficiency of operation is improved.

Spent clay may be regenerated by roasting in a furnace at 900-1000°F. Clays of the fuller's earth type are considered best.[189] The use of copper oxide in conjunction with the clay is said to effect sweetening of the distillate and also to accelerate the removal of gum-forming constituents.[190] By mixing 5 to 25 per cent of a filter aid, such as kieselguhr, deeper beds of catalyst may be employed and better drainage of the polymers is said to result.[191]

A variation in the procedure, consisting in employing a two-step process, has been proposed. For example, gasoline is first treated in the vapor phase and then in the liquid phase with fresh adsorbent.[192] The fuller's earth may be kept in motion by a stream of gases of sufficient velocity to suspend the material in the heating zone.[193] Wells[194] suggested mixing cracked naphtha with a slurry of clay in gas oil under pressure. Thus, 5 to 20 per cent of the slurry (containing 1 to 4 per cent of clay and the remainder gas oil) is mixed with the crude naphtha, and passed through a tube heated to 350-600°F. The products are vaporized and fractionated, removing the gas oil and solid adsorbent clay while the naphtha is still maintained in the vapor phase. The purified material is subsequently condensed and the mixture of gas oil and clay is returned to the system.

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to Texas Co.; *Chem. Abs.*, 1934, **28**, 4898; *J. Inst. Pet. Tech.*, 1934, **20**, 503A. R. J. Dearborn and W. M. Stratford, U. S. P. 2,028,100, Jan. 14, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 1551; *J. Inst. Pet. Tech.*, 1936, **22**, 157A. J. M. Wadsworth, U. S. P. 1,960,561, May 29, 1934; *Brit. Chem. Abs.* **B**, 1935, 295; *J. Inst. Pet. Tech.*, 1934, **20**, 459A; *Chem. Abs.*, 1934, **28**, 4587. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, **1934**.

[186] T. T. Gray, U. S. P. 2,034,575, Mar. 17, 1936, to Gray Process Corp.; *Chem. Abs.*, 1936, **30**, 3206; *J. Inst. Pet. Tech.*, 1936, **22**, 211A.

[187] H. M. Steininger, *Ind. Eng. Chem.*, 1934, **26**, 1039; *Chem. Abs.*, 1934, **28**, 7504; *Brit. Chem. Abs.* **B**, 1935, 886.

[188] M. R. Mandelbaum, *Proc. World Petroleum Congr. London*, 1933, **2**, 21; *Chem. Abs.*, 1934, **28**, 4878; *Brit. Chem. Abs.* **B**, 1934, 1045. See also M. R. Mandelbaum and P. F. Swanson, *Oil Gas J.*, 1936, **34** (52), 226; *Chem. Abs.*, 1936, **30**, 5756.

[189] Certain Ural clays, silica gel and charcoal have also been recommended. See I. J. Postovski and S. P. Tzikin, *J. Applied Chem.* (*U.S.S.R.*), 1936, **9**, 61; *Brit. Chem. Abs.* **B**, 1936, 435; *Chem. Abs.*, 1936, **30**, 5756; and U. B. Bray, R. C. Pollock and D. R. Merrill, U. S. P. 1,981,305, Nov. 20, 1934, to Union Oil Co. of California; *Brit. Chem. Abs.* **B**, 1935, 983; *Chem. Abs.*, 1935, **29**, 589. The use of "Gumbrin" (a Russian clay) has been reported by L. Gukhman, A. Degtyareva and A. Nagiev, *Azer. Neft. Khoz.*, **1935** (12), 60; *Chem. Abs.*, 1936, **30**, 8587. R. E. Manley and W. Ullrich (U. S. P. 2,054,774, Sep. 15, 1936, to Texas Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 546A; *Chem. Abs.*, 1936, **30**, 7834) use acid-treated montmorillite clay, 50 per cent of which is finer than 200 mesh. 3576.

[190] T. T. Gray, U. S. P. 1,952,751, Mar. 27, 1934, to Gray Process Corp.; *Chem. Abs.*, 1934, **28**, 3576.

[191] R. E. Manley and W. Ullrich, Canadian P. 343,990, 1934, to Texaco Development Corp.; *Chem. Abs.*, 1934, **28**, 7516.

[192] M. R. Mandelbaum, U. S. P. 1,965,105, July 3, 1934, to Gray Process Corp.; *Chem. Abs.*, 1934, **28**, 5657; *J. Inst. Pet. Tech.*, 1934, **20**, 537A.

[193] T. T. Gray, U. S. P. 2,020,115, Nov. 5, 1935, and J. B. Hill, U. S. P. 2,039,904, May 5, 1936. Both to Gray Process Corp.; *Chem. Abs.*, 1936, **30**, 603, 4308; *J. Inst. Pet. Tech.*, 1936, **22**, 23A, 304A. See also W. S. Baylis, U. S. P. 1,949,673, Mar. 6, 1934, to Patco, Inc.; *Brit. Chem. Abs.* **B**, 1935, 55; *Chem. Abs.*, 1934, **28**, 2885; *J. Inst. Pet. Tech.*, 1934, **20**, 375A.

[194] A. A. Wells, U. S. P. 2,036,166, Mar. 31, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 3630; *J. Inst. Pet. Tech.*, 1936, **22**, 214A.

Lachman Process. According to Lachman[195] this process consists in washing the hydrocarbon vapors with a hot concentrated solution of zinc chloride (50 per cent). The presence of large quantities of hydrogen sulphide adversely affects the operation. The vapors are usually stabilized before the treatment. In practice, the vapors to be treated, together with superheated steam, are passed countercurrent to the zinc chloride through a series of bubble towers.[196] The actual zinc chloride consumption ranges from 0.3 to 1 lb. per barrel of gasoline treated. The gasoline loss is reported as very low.[197]

Andreev proposed a variation of this method which involved the use of zinc chloride deposited on Raschig rings, pumice stone or gumbrin (a Russian clay).[198] Experiments on the refining of crude benzol and toluol in this manner were not very successful. However, it was pointed out that after this preliminary treatment with zinc chloride, 40 per cent less acid was required in the subsequent acid washing.[199] The use of pressure in conjunction with zinc chloride is advocated by Zadolin and Butkov.[200]

Day Process. This comprises treating hydrocarbons, in either the liquid or vapor phase, with aqueous hydrochloric acid in the presence of a free metal. Zinc, copper, aluminum, iron, tin and various alloys, such as brass, are used.[201] As an illustration of one mode of procedure, stabilized gasoline distillate is heated to the required temperature and charged into an acid-proof treating chamber, where it is mixed with dilute hydrochloric acid. The heated distillate and acid are contacted by upward flow through brass packing and then discharged into a fractionating column, where the polymers are separated. The distillate is neutralized with ammonia immediately after leaving the column. Polymerization losses of less than 1 per cent are reported, using this process.

Other Methods of Refining. As is well known, sulphuric acid has been used quite extensively as a refining agent, but since it will react with olefins, aromatics, naphthenes and even paraffins under certain conditions,[202] its use in this way is being more and more replaced by other substances which do not bring about such large losses in the purified product. Sager has listed the chief factors in the sulphuric acid operation as (1) concentration of acid employed, (2) amount of acid, (3) temperature at which the treatment is carried out and (4) the time of contact between the acid and oil.[203] Using 2 per cent by weight of concentrated sulphuric acid (98 per cent), the diolefins and most of the unstable olefins were removed in 5 to 25 seconds with intimate contact. Using more acid, the contact time could be reduced, and the inverse was true with smaller amounts of acid. The speed of polymerization of the olefins is rapid up to 80 seconds, but at 100 seconds can hardly be detected. The polymerization losses varied from 0.6 to 1.1 per cent for short periods and 1.8 to 5.5 per cent for the longer times. Sager found that chiefly the unsaturates were removed, the aromatics being only slightly affected, and the naphthenes and paraffins not at all during the above operations.[204]

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[195] A. Lachman, *World Petroleum*, 1934, **5** (10), 384; *J. Inst. Pet. Tech.*, 1935, **21**, 95A.

[196] A. Lachman, U. S. P. 1,790,622, Jan. 27, 1931, and 1,809,170, July 19, 1931, both to Richfield Oil Co. of California; *Chem. Abs.*, 1931, **25**, 1374, 4395; *Brit. Chem. Abs.* B, 1931, 1038. U. S. P. Re. 19,879, Mar. 3, 1936, 2,035,607 and 2,035,608, Mar. 31, 1936, all to Vapor Treating Processes Inc.; *Chem. Abs.*, 1936, **30**, 2743, 3626; *J. Inst. Pet. Tech.*, 1936, **22**, 214A.

[197] J. C. Albright, *Refiner*, 1933, **12**, 298; *J. Inst. Pet. Tech.*, 1933, **19**, 427A; *Chem. Abs.*, 1933, **27**, 5526.

[198] I. Andreev, *Trans. 1st All-Union Meeting Sci.-Eng.-Tech. Soc. Petroleum Workers, Baku*, **1933**, *Gosud. Nauch. Tekh. Gorno-Geol. Neft. Izdat*, **1934**, (3), 236; *Chem. Abs.*, 1935, **29**, 4559; *Brit. Chem. Abs.* B, 1936, 227. Ferrous chloride may be substituted in place of zinc chloride. See K. S. Kuruindin and I. I. Ivanov, *Khim. Tverdogo Topliva*, 1934, **4**, 578; *Chem. Abs.*, 1934, **28**, 6281; *Brit. Chem. Abs.* B, 1935, 54.

[199] S. N. Popov and S. I. Polonskaya, *Neft. Khoz.*, 1933, **25**, 93; *Chem. Abs.*, 1934, **28**, 2338; *Brit. Chem. Abs.* B, 1934, 613; *J. Inst. Pet. Tech.*, 1934, **20**, 415A. See also A. Demchenko, *Neft.* 1932, **3** (23-24), 14; *Chem. Abs.*, 1935, **29**, 5257; *Brit. Chem. Abs.* B, 1936, 403.

[200] S. A. Zadolin and N. A. Butkov, *Neft. Khoz.*, 1933, **24**, 34; *Chem. Abs.*, 1933, **27**, 5952; *Brit. Chem. Abs.* B, 1934, 261.

[201] R. B. Day, U. S. P. 1,920,247 and 1,920,248, Aug. 1, 1933; 1,937,873, Dec. 5, 1933; *Brit. Chem. Abs.* B, 1934, 440, 870; *Chem. Abs.*, 1933, **27**, 4916; 1934, **28**, 1179. U. S. P. 1,970,281, 1,970,282, 1,970,283, 1,970,284, Aug. 14, 1934; 2,001,185, May 14, 1935; 2,029,256, Jan. 28, 1936; 2,029,757 and 2,029,758, Feb. 4, 1936; *Chem. Abs.*, 1934, **28**, 6295; 1935, **29**, 4572; 1936, **30**, 1987, 1990, 1991; all to Universal Oil Products Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 538A; 1935, **21**, 266A; 1936, **22**, 158A, 213A.

[202] J. C. Morrell and G. Egloff, *Nat. Pet. News*, 1936, **28** (12), 33, (13), 24G, (15), 24L, (16), 37; *Chem. Abs.*, 1936, **30**, 4656; *J. Inst. Pet. Tech.*, 1936, **22**, 265A, 309A.

[203] F. Sager, *J. Inst. Pet. Tech.*, 1934, **20**, 138; *Brit. Chem. Abs.* B, 1934, 308; *Chem. Abs.*, 1934, **28**, 3571. See also V. A. Kalichevsky and B. A. Stagner, "Chemical Refining of Petroleum," Reinhold Publishing Corp., New York, 1934.

De Florez[205] recommends the use of reduced pressure to effect cooling during the acid treatment. The more reactive gum forming constituents may be polymerized by the addition of a small quantity of acid, and can be withdrawn in the form of an acid sludge.[206] Ipatieff proposes to use acid sludge material from treating cracked products for refining. By interaction of the olefins and the acid sludge, alkylated compounds are formed, thus increasing the antiknock value of the gasoline.[207] By boiling kerosene with sulphuric acid, Ciochina also noted some degree of polymerization. In this instance oxidation occurred, as carbon was deposited, while with an excess of acid both carbon monoxide and dioxide were given off. The amount of high-boiling residue was considerably increased.[208]

Refining with adsorptive clay[209] may also be carried out in the liquid phase. Temperatures of 149-232°C. and 250 lbs. per sq. in. pressure or 315-370°C. and 1000 lbs. pressure are recommended for this type of treatment.[210] Dry copper silicate[211] can be substituted as contact agent in place of clay[212]

Molten selenium at 400-600°C. and 300 lbs. pressure[213] and sodium at 800-900°F. and reduced pressure[214] have been suggested as catalysts. Bruzac reports that the unstable constituents are polymerized readily by exposing the crude gasoline to sun or artificial radiations.[215]

Vapor phase refining may also be effected in a number of ways. Greensand[216] in the presence of hydrochloric acid or steam and hydrochloric acid, phosphorus pentoxide deposited on coke[217] and mixtures of clay and calcium oxide and sodium

[204] According to E. Wendehorst and E. Knoche (*Angew. Chem.*, 1934, **47**, 43; *Brit. Chem. Abs.* **B**, 1934, 179; *Chem. Abs.*, 1934, **28**, 2172) benzene is completely sulphonated by 100 per cent sulphuric acid after 1 hour's standing. Olefins, such as pentene, undergo partial sulphonation and partial polymerization, but paraffins and naphthenes are unaffected by this treatment. See also Chapters 46 and 50.

[205] L. de Florez, U. S. P. 1,956,525, Apr. 4, 1934; *Chem. Abs.*, 1934, **28**, 4218; *Brit. Chem. Abs.* **B**, 1935, 135; *J. Inst. Pet. Tech.*, 1934, **20**, 426A.

[206] E. B. Miller and G. C. Connolly, U. S. P. 1,939,129, Dec. 12, 1933, to the Silica Gel Corp.; *Chem. Abs.*, 1934, **28**, 1521; *J. Inst. Pet. Tech.*, 1934, **20**, 113A.

[207] V. N. Ipatieff, U. S. P. 2,001,906, 2,001,907, 2,001,908, 2,001,909, 2,001,910, May 21, 1935, all to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 4573; *J. Inst. Pet. Tech.*, 1935, **21**, 267A.

[208] I. Ciochina, *Petroleum Z.*, 1933, **29** (33), 1; *Chem. Abs.*, 1934, **28**, 621; *Brit. Chem. Abs.* **B**, 1933, 901.

[209] S. N. Popov and A. E. Beilin (*Azer. Neft. Khoz.*, 1935, **5**, 98; *J. Inst. Pet. Tech.*, 1936, **22**, 321A; *Chem. Abs.*, 1936, **30**, 4022) have applied the clay refining principle to polymerization of olefins in cracked crude oil in the preparation of synthetic drying oils.

[210] W. M. Stratford, U. S. P. 2,034,317, Mar. 17, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 3206; *J. Inst. Pet. Tech.*, 1936, **22**, 213A. D. M. Evans and W. C. Dorsett, U. S. P. 1,957,449, May 8, 1934, to Petroleum Conversion Corp.; *J. Inst. Pet. Tech.*, 1934, **20**, 459A; *Chem. Abs.*, 1934, **28**, 4220. British P. 437,023, 1935, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1936, 8. W. F. Faragher and E. J. Houdry, U. S. P. 2,035,467, Mar. 31, 1936, to Houdry Process Corp.; *Chem. Abs.*, 1936, **30**, 3629; *J. Inst. Pet. Tech.*, 1936, **22**, 261A.

[211] In some instances, silicic acid has been proposed. *Cf.* E. Erdheim, *Petroleum Z.*, 1936, **32** (20), 1; *Chem. Abs.*, 1936, **30**, 7827; *J. Inst. Pet. Tech.*, 1936, **22**, 302A.

[212] W. A. Smith, U. S. P. 1,964,087, June 26, 1934; *Brit. Chem. Abs.* **B**, 1935, 394; *Chem. Abs.*, 1934, **28**, 5224.

[213] C. C. Towne, U. S. P. 1,997,159, Apr. 9, 1935, to Texas Co.; *Brit. Chem. Abs.* **B**, 1936, 358; *Chem. Abs.*, 1935, **29**, 3821.

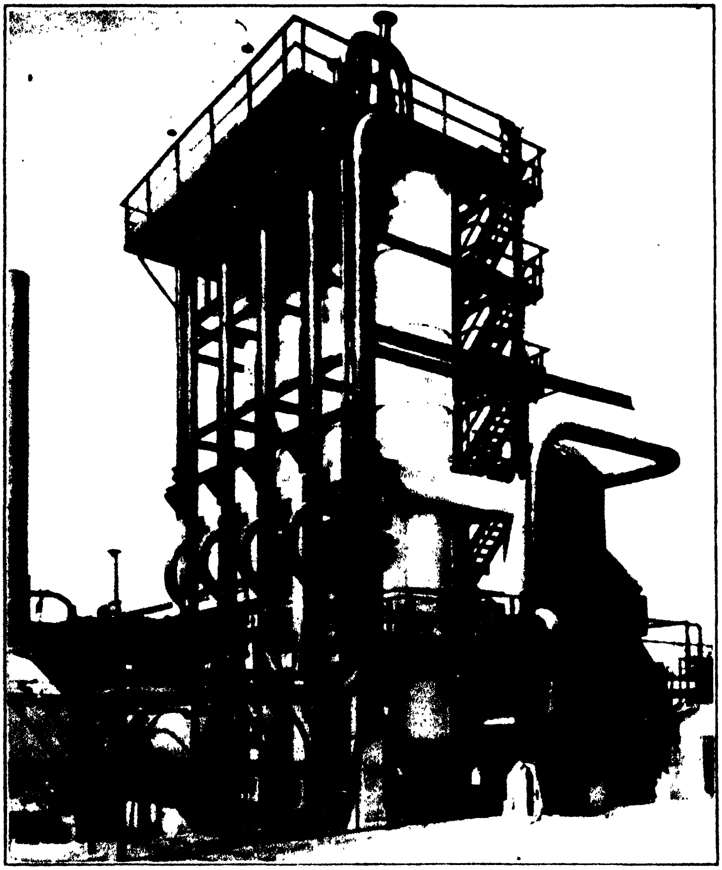
[214] W. M. Stratford, Canadian P. 356,957, 1936, to Texaco Development Corp.; *Chem. Abs.*, 1936, **30**, 3628. See also R. S. Vose, U. S. P. 1,962,698, June 12, 1934, to E. I. du Pont de Nemours & Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 504A; *Chem. Abs.*, 1934, **28**, 4897.

[215] J. F. A. Bruzac, French P. 766,060, 1934; *Chem. Abs.*, 1934, **28**, 7517.

[216] C. D. Lowry, U. S. P. 1,947,749, Mar. 6, 1934, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1935, 55; *Chem. Abs.*, 1934, **28**, 2888.

[217] B. W. Malishev, *Ind. Eng. Chem.*, 1936, **28**, 190; *Brit. Chem. Abs.* **B**, 1936, 307; *J. Inst. Pet. Tech.*, 1936, **22**, 155A.

hydroxide[218] have all been investigated. Morrell[219] has advocated the use of heavy metal salts in the presence of a small amount of acid to prevent hydrolysis (e.g., ferric chloride and hydrochloric acid or zinc sulphate and sulphuric acid). Sulphonic acids, dissolved or suspended in inert organic mediums, may also be used as catalysts for the vapor phase treatment.[220]



Courtesy Universal Oil Products Co

FIG. 149.—Catalytic Polymerization Plant. Daily capacity, 8 million cu. ft. of gas.

Egloff reports that the addition of hydrogen to the hydrocarbon vapors under high pressure and moderate temperatures, in the presence of zinc chloride solution, produces a substantial saturation of the olefins in the cracked vapors.[221] This manner of treatment is reported to be effective for desulphurizing high sulphur-content oils, such as certain Mexican gas oils. Thus, Egloff suggests mixing the cracked gas oil vapors at 510°F. and 220 lbs. per sq. in. pressure with hydrogen and bubbling the gas through zinc chloride solution. Both hydrogenation and polymerization of the cracked vapors is said to result. Heat treatment with oxygen, under pressure, is also suggested to eliminate gum forming substances.[222]

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[218] C. E. Dolbear, U. S. P. 2,034,712, Mar. 24, 1936, to P. Wiseman, P. K. Wiseman and C. E. Dolbear; *J. Inst. Pet. Tech.*, 1936, **22**, 214A; *Chem. Abs.*, 1936, **30**, 3215.

[219] J. C. Morrell, U. S. P. 1,988,083 and 1,988,084, Jan. 15, 1935, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1935, 1083; *Chem. Abs.*, 1935, **29**, 1618.

[220] British P. 437,864, 1935, to N. V. Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1936, 53; *J. Inst. Pet. Tech.*, 1936, **22**, 54A; *Chem. Abs.*, 1936, **30**, 2745.

[221] G. Egloff, U. S. P. 2,009,879, July 30, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 6414; *J. Inst. Pet. Tech.*, 1935, **21**, 381A.

SYNTHETIC LUBRICATING OILS

Another commercial application of polymerization is in the production of synthetic lubricants.[223] The work of earlier investigators[224] in this field indicated that lubricants obtained catalytically from ethylene had a very inferior viscosity-temperature coefficient. It was further established that the viscosity indices increased proportionally to the length of the straight carbon chain in the starting material.[225] Atkinson and Storch,[226] therefore, deemed it advisable to use a two-stage process, first thermally polymerizing the ethylene to a liquid boiling in the gasoline range and then further condensing this material with aluminum chloride to a viscous liquid of the "light" lubricant type. Thermal treatment was carried out at 370-395°C. and 50 to 70 kg. per sq. cm. pressure, and catalytic reaction was effected at room temperature with continuous agitation for 48 hours. The washed oil had viscosities of 155-208 seconds at 100°F. and 44-46 at 210°F. (Saybolt). Removal of the lighter ingredients (33 per cent) by vacuum distillation resulted in an oil with a viscosity of 532-710 seconds at 100°F. and 58.5-65 at 210°F. and a pour point of —20°F. Polymerization of ethylene at 100-300°C. and high pressure with a catalyst of aluminum chloride and aluminum has been reported to give products with viscosity indices of 60-70, whereas when aluminum chloride alone is used, the results are poor.[227] On the other hand, Koch has stated that synthetic material obtained using aluminum chloride at 130°C. is equal to, or better than, the natural product.[228]

Condensation of distillation products with aluminum chloride is generally carried out in two separate operations. In the first step, the more unsaturated hydrocarbons are polymerized to form a "mud" by means of the addition of a small amount of the catalyst. The remaining material is freed from this mud (by distillation or by means of solvents) and then subsequently treated with more of the catalyst.[229]

Wax-free lubricants may be obtained by the vapor-phase cracking of petroleum distillates.[230] For instance, at 540-700°C., gas oil yields a product which on redistillation has a viscosity of 200-600 seconds (Saybolt) at temperatures of 60° and 38°C., respectively.[231] Gaseous olefins may be converted to liquids of a viscosity index in excess of 100 by heating at 675° to 725°F. under 3000 lbs. per sq. in. pressure with heating times of 100 minutes or more.[232] Wiezevich and Whiteley recommend the addition of air in the treatment to form oxygenated products.[233] Lower olefins, such as ethylene, propene or butene, are preheated to about 310°C. under pressure, and mixed with small amounts of air. In addition to exerting a catalytic polymerizing action on the olefins, the oxygen is said to enter into combination with the polymers. Sulphuric acid, phosphoric acid,[233a] amines and other organic bases or nitrites[233b] have also been suggested as catalysts for the condensation. Olefins available for polymerization to synthetic lubricating oils are obtained by Loebel[233c] by cracking a paraffinic oil under pressure in the liquid phase, subsequently removing any resulting aromatic hydrocarbons and subjecting the remainder of the product to vapor-phase cracking.

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[222] C. P. Wilson, Jr., U. S. P. 1,935,967, Nov. 21, 1933, to Texas Co.; *J. Inst. Pet. Tech*, 1934, **20**, 38A; *Chem. Abs.*, 1934, **28**, 890

[223] A more extensive discussion of the use of aluminum chloride is given in Chapter 6.

[224] A. W. Nash, H. M. Stanley, A. R Bowen, *J. Inst. Pet. Tech.*, 1930, **16**, 830; *Chem. Abs.*, 1931, **25**, 1664; *Brit. Chem. Abs.* **B**, 1931, 328. F. W. Sullivan, Jr., V. Voorhees, A. W. Neeley and R. V. Shankland, *Ind. Eng. Chem.*, 1931, **23**, 604; *Brit. Chem Abs.* **B**, 1931, 708; *Chem. Abs.*, 1931, **25**, 3476. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[225] See Chapter 1.

[226] R. G. Atkinson and H. H. Storch, *Ind. Eng. Chem.*, 1934, **26**, 1120; *Chem. Abs.*, 1934, **28**, 7508; *Brit. Chem. Abs.* **B**, 1935, 889.

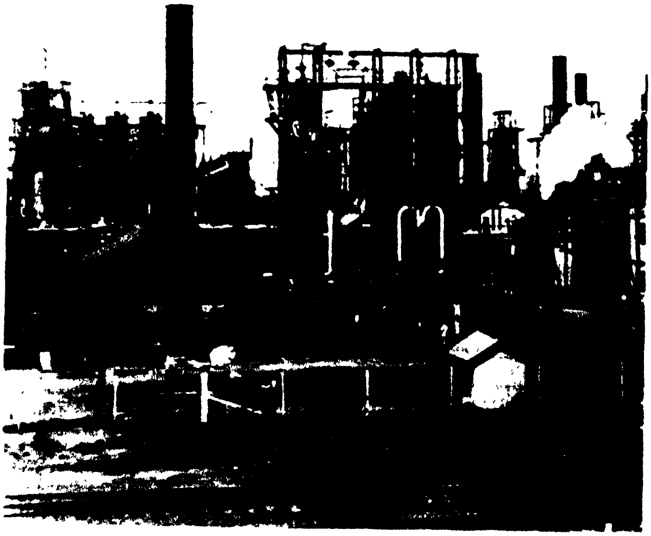
[227] F. C. Hall, W. R. Wiggins and A. W. Nash, *J. Inst. Fuel*, 1935, **9**, 106; *Brit Chem. Abs.* **B**, 1936, 227; *Chem. Abs.*, 1936, **30**, 5021.

[228] H. Koch, *Z. Ver. deut. Ing.*, 1936, **80**, 49; *Chem Abs.*, 1936, **30**, 2741.

[229] M. Pier and F. Christmann, U. S. P. 1,965,390, July 3, 1934; *Chem. Abs.*, 1934, **28**, 5657; *J. Inst. Pet. Tech.*, 1934, **20**, 539A. H. Zorn and W. Rosinski, German P. 593,455, 1934; *Chem. Abs.*, 1934, **28**, 3229, both to I. G. Farbenind A.-G. French P. 761,417, 1934, and 775,701, 1935, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 4219; 1935, **29**, 3150. Dutch P. 36,948, 1935; *Chem. Abs.*, 1936, **30**, 2743; *J. Inst. Pet. Tech.*, 1935, **21**, 176A.

[230] R. C. Osterstrom, U. S. P. 1,955,596, Apr. 17, 1934, to Pure Oil Co.; *Chem. Abs.*, 1934, **28**, 3889; *J. Inst. Pet. Tech.*, 1934, **20**, 427A; *Brit. Chem. Abs.* **B**, 1935, 261.

[231] V. V. Orzhekhovskii (Russian P. 35,429, 1934; *Chem. Abs.*, 1936, **30**, 2430) has described a viscosimeter equipped with a rotating core for the continuous observation of the polymerization of oils.



Courtesy Industrial and Engineering Chemistry

FIG. 150.—Cracking Equipment in a Louisiana Petroleum Refinery.

SYNTHETIC RUBBER BY POLYMERIZATION OF BUTADIENE

Since 1930, the production of synthetic rubber by polymerization of butadiene has developed rapidly in Russia. Bridgwater[233d] has stated that 20,000 tons were produced in that country during the first ten months of 1935. In the entire year of 1934, the total output was only 11,300 tons. No information as to the cost is available, but it seems apparent from the yields quoted and statistics on the number of workers employed in the industry that the cost of the product is many times greater than that of natural rubber.

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[232] H. E. Batchelder and W. E. Kuentzel, Canadian P. 345,543, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 2346. See also French P. 800,185, 1936, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 8597.

[233] P. J. Wiezevich and J. M. Whiteley, U. S. P. 1,981,819, Nov. 20, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 474; *Brit. Chem. Abs.* B, 1935, 881.

[233a] British P. 411,158, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 6562; *J. Inst. Pet. Tech.*, 1934, **20**, 459A.

[233b] British P. 435,598, 1935, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech.*, 1935, **21**, 459A; *Brit. Chem. Abs.* B, 1935, 1127.

[233c] A. Loebel, U. S. P. 2,051,612, Aug. 18, 1936, to Shell Development Co.; *J. Inst. Pet. Tech.*, 1936, **22**, 451A; *Chem. Abs.* 1936, **30**, 6939.

[233d] F. R. Bridgwater, *Ind. Eng. Chem.*, 1936, **28**, 394; *Chem. Abs.*, 1936, **30**, 3679; *Brit. Chem.*

The butadiene used in this industry is derived by the pyrolysis of either petroleum fractions or ethyl alcohol.[233e] The first of these methods has been discussed by Buizov.[233f] In practice, the petroleum vapors are heated to 300-400°C., and then passed through a short heater, where cracking takes place at 700-800°C. and a pressure of 70-90 mm. The gases are expanded immediately after heating, then thoroughly cooled, liquefied by compression and fractionally distilled. Decomposition and condensation of the butadiene formed is avoided by the control of temperature, pressure and velocity of the vapors through the reaction zone. Yields as high as 16 to 17 per cent of butadiene are stated to be obtained in this manner. Table 144 shows the yield of products resulting when using raw materials on a semi-commercial scale under the above conditions.

TABLE 144.—*Products Obtained by Pyrolysis of Petroleum Fractions.*

Petroleum Fraction	Butadiene, %	Gas, cu.m./kg. Oil	Tar, g./kg. Oil
Crude Oil	10-11	1.10	—
Kerosene	11-12	0.67	150-180
Machine oil	11	0.68	150
Transformer oil	11	0.64	180
2nd grade gasoline	12-15	1.05	20
Naphtha	10	0.79	30
1st grade gasoline	15	0.75	70-90
Fuel oil	10	0.51	190

Butadiene may be separated from the other resultants by absorption in benzene, kerosene, absolute alcohol, water or gasoline, or by compression. Kerosene and water remove the most, but the former solvent may retain as much as 50 per cent of the hydrocarbon, which cannot be recovered. The compression method is reported as giving a stock of variable composition. Polymerization is carried out in autoclaves (lined with hard rubber) in the presence of 1 per cent of diazoaminobenzene as catalyst. Optimum conditions for this step are given as 100°C. and 18 atmospheres, and yields of 50 per cent of "butadiene rubber" are obtained after 6 to 12 days under these conditions. The residue from the operation consists of unreacted butadiene, some dimer and also small amounts of butene.

The preparation of butadiene from ethyl alcohol has already been discussed.[233g] The polymerization of this product, which is much purer than that obtained from petroleum cracking, is carried out on a commercial scale at 50-60°C. and 4 atmospheres, using metallic sodium as a catalyst.[234] The reaction takes place in both the gaseous and liquid phases, and is heterogeneous. At a given pressure, the rate is the same in both phases. After an initial period of acceleration, the speed slows down to a constant rate, due perhaps to the formation of primary sodium compounds. Polymerization is thought to proceed by the successive addition of mono-

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Abs. B, 1936, 705. See also Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, *1935*, for a discussion of synthetic rubber.

[233e] M. A. Lur'e and V. A. Ignatyuk, *Sintet. Kauchuk*, **1932** (3), 12; *Chem. Abs.*, 1933, **27**, 6016; *Brit. Chem. Abs.* B, 1934, 232. See also Chapter 4.

[233f] B. V. Buizov, *J. Applied Chem. (U.S.S.R.)*, 1933, **6**, 1074; *Foreign Petroleum Tech.*, 1934, **2**, 185, 213; *Chem. Abs.*, 1934, **28**, 5711; *Brit. Chem. Abs.* B, 1934, 245. See also I. G. Akobzahanov, *Rev. gen. mat. plastiques*, 1934, **10**, 370; *Rubber Age*, 1935, **16**, 14; *Chem. Abs.*, 1935, **29**, 3872.

[233g] See Chapter 4.

[234] M. A. Lur'e and V. A. Ignatyuk, *loc. cit.*

meric molecules to these sodium compounds.[235] Mixed catalysts of sodium and iron oxide and sodium and magnesium oxide have also been investigated.[236]

Vulcanization of the polymerized product with sulphur is said to be much smoother than with the natural rubber. The technical treatment is the same. The properties of the synthetic product are reported as being satisfactory enough to serve as a substitute for rubber in many cases,[237] in fact, the claim is made that it is even stronger than the ordinary rubber.[238] The material is being used for tires,[239] rubber soles and heels, ebonite goods, raincoat cloth,[240] gasoline hose and tire tubes.[241]

OTHER USES OF POLYMERIZATION PRODUCTS

Many proposals have been made to utilize the numerous products of polymerization reactions besides those previously mentioned. Waste gases may be converted into illuminating gas by subjecting them to cracking at above 500°C., to enrich the olefin content.[242] The higher polymers of isobutene are recommended in making safety glass, plywood, adhesive plaster,[243] flypaper,[244] greases, lubricating and insulating oils,[245] chewing gum, wax for sealing tree wounds, a decay preventative,[246] and cleansing compounds.[247]

Bodies resulting from the polymerization of diolefins may be added to lubricating oils to improve the viscosity of the latter.[248] Other suggested uses are as rubber substitutes,[249] vulcanizable products,[249a] insulators[249b] and coating compositions.[250] The low-boiling ends of refinery gasoline (boiling below 21°C.) may be treated catalytically to form isoparaffinic hydrocarbons which may be employed to increase the viscosity of oils.[251] Using metallic halides (such as aluminum chloride) as the catalyst, at 38°C. these low-boiling fractions (containing isobutene) are converted to solids of a molecular weight greater than 800. Similarly, at slightly lower temperatures (27°C.) the polymer has a molecular weight of 4000 to 10,000. About 0.5 to 5 per cent by weight of this substance is usually blended with the lubricating oil. Hydrocarbons of this nature have been stated to increase the viscosity index of an oil from 93 to 120. On the other hand, liquid polymers have also been recommended as diluents in order to increase the fluidity of various oils obtained from lignite tar oils.[252] Products with molecular weights of 800 to 2000 may be added to greases and solid lubricants.[253] High-pressure condensation of cracked gasoline results in a liquid polymer which is reported to be a plasticizer[254] or a softener[255] for rubber. Cracked petroleum distillates may be polymerized to give higher boiling hydrocarbons which may be incorporated into synthetic resins[256] or oxidized with air, sulphur or chlorine to form asphaltic[257] and insulating[258] materials.

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[235] A. Abkin and S. Medvedev, *Trans. Faraday Soc.*, 1936, **32**, 286; *Brit. Chem. Abs.* **A**, 1936, 296; *Chem. Abs.*, 1936, **30**, 2472.

[236] V. E. Kravetz, *Sintet. Kauchuk*, **1935**, 4 (1), 36; *Chem. Abs.*, 1935, **29**, 4627; *Brit. Chem. Abs.* **B**, 1936, 229.

[237] I. I. Zhukov, V. A. Komarov, S. F. Val'ter and E. I. Gribova, *Sintet. Kauchuk*, **1936**, (2), 4; *Chem. Abs.*, 1936, **30**, 5069.

[238] S. V. Lebedev, S. A. Subbotin, T. L. Zingerevich and V .D. Strebkov, *Trudui Gosudarst. Opuit. Zavoda Sintet. Kauchuka Litera B. III. Synthetic Rubber*, **1934**, 100; *Chem. Abs.*, 1936, **30**, 5451. S. V. Lebedev, S. A. Subbotin and V. F. Evstratov, *ibid.*, **1934**, 85; *Chem. Abs.*, 1936, **30**, 5451 See also F. Kirchhof, *Tropenpflanzer*, 1934, **37**, 505; *Chem. Abs.*, 1935, **29**, 8400. See also I. I. Zhukov, V. A. Komarov, E. I. Gribova and N. L. Selivanova, *Sintet. Kauchuk*, **1936** (4), 4; *Chem. Abs.*, 1936, **30**, 6602. B. Y. Osipovskii, *Sintet. Kauchuk*, **1936** (4), 22; *Chem. Abs.*, 1936, **30**, 6602. G. I. Glazunov, *J. Rubber Ind. (U.S.S.R.)*, 1935, **12**, 910; *Chem. Abs.*, 1936, **30**, 5454. B. Fabritziev and G. Buiko, *J. Rubber Ind. (U.S.S.R.)*, **1936**, 141; *Chem. Abs.*, 1936, **30**, 6603.

[239] F. Merzlikin, *J. Rubber Ind. (U.S.S.R.)*, 1935, **12**, 518; *Chem. Abs.*, 1935, **29**, 7118.

[240] P. Kaplin, *J. Rubber Ind. (U.S.S.R.)*, 1935, **12**, 953; *Chem. Abs.*, 1936, **30**, 5454; *Brit. Chem. Abs.* **B**, 1936, 655.

[241] B. V. Buizov, *loc. cit.* Z. Koryushenko and M. Ivanova, *J. Rubber Ind. (U.S.S.R.)*, 1935, **12**, 951; *Chem. Abs.*, 1936, **30**, 5454. N. Chesnokov, *ibid.*, **1936**, 452; *Chem. Abs.*, 1936, **30**, 5454.

[242] French P. 765,425, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 6985.

[243] French P. 775,306, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 2625

[244] British P. 437,704, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1936, 97.

[245] British P. 399, 527, 1933, to I. G. Farbenind. A-G.; *Chem. Abs.*, 1934, **28**, 2518; *Brit. Chem. Abs.* **B**, 1933, 997. See also J. C. Zimmer and E. W. Carlson, U. S. P. 2,074,039, March 16, 1937, to Standard Oil Development Co.

[246] British P. 439,899, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 3549.

[247] German P. 623,924, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 4953.

[248] British P. 411,893 and 411,894, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, **B**, 1934, 749. French P. 758,269, 1934; *Chem. Abs.*, 1934, **28**, 3230. Austrian P. 138,763, 1933; *J. Inst. Pet. Tech.*, 1934, **20**. 617A.

[249] French P. 787,467, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 2047.

[249a] French P. 788,973, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 2043.

[249b] French P. 788,840, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 2044.

[250] C. A. Thomas. U. S. P. 1,947,626, Feb. 20, 1934, to Dayton Synthetic Chemicals, Inc.; *Chem. Abs.*, 1934, **28**, 2927; *Brit. Chem. Abs.*, **B**, 1934, 1071. See Chapter 6. Also Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, 1934; and "The Chemistry of Synthetic Resins." Reinhold Publishing Corp., New York, 1935.

[251] F. A. Howard, U. S. P. 2,049,062, July 28, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 6537. British P. 437,934, 1935; *Chem. Abs.*, 1936, **30**, 2746; *Brit. Chem. Abs.* **B**, 1936, 54; *J. Inst. Pet. Tech.*, 1936, **22**, 58A. British P. 455,114, 1936; *Brit. Chem. Abs.* **B**, 1936, 1191; *J. Inst. Pet. Tech.*, 1937, **23**, 201A. French P. 771,272, 1934; *Chem. Abs.*, 1935, **29**, 919. French P. 798.929, 1936 and 801,715, 1936; *Chem. Abs.*, 1936, **30**, 7836; 1937, **31**, 536. M. Otto, F. L. Miller, A. J. Blackwood and G. H. B. Davis, *Oil Gas. J.*, 1934, **33** (26), 98; *Refiner*, 1934, **13**,

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411; *Chem. Abs.*, 1935, **29**, 587; *J. Inst. Pet. Tech.*, 1935, **21**, 68A. See also *Nat. Pet. News*, 1934, **26** (46), 30; *J. Inst. Pet. Tech.*, 1935, **21**, 61A. "Exanol" and "Vistanex" (the latter is applied to the highest molecular weight products) are trade names for these substances.

[252] French P. 43,093, 1934; 762,289, 1934; and 762,381, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5225, 4592, 4576.

[253] British P. 379,717, 1932, and 401,295, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1932, 971; 1934, 184.

[254] J. Hyman, Canadian P. 354,966, 1935, to Velsicol Corp.; *Chem. Abs.*, 1936, **30**, 2046.

[255] A. Y. Larin, *Neft. Khoz*, 1935, **28** (6), 57; *Chem. Abs.*, 1936, **30**, 3990; *J. Inst. Pet. Tech.*, 1936, **22**, 156A.

[256] F. A. Apgar and A. Runyan, U. S. P. 1,945,719, Feb. 6, 1934, to Sinclair Oil Refining Co.; *Chem. Abs.*, 1934, **28**, 2556; *Brit. Chem. Abs.* **B**, 1935, 1022.

[257] French P. 793,501, 1936, to Standard Oil Co. of California; *Chem. Abs.*, 1936, **30**, 4664.

[258] M. Pier and F. Christmann, German P. 594,167, 1934, to I. G. Farbenind. A-G.; *Chem. Abs.*, 1934, **28**, 3576.

Chapter 27

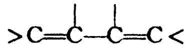
Some Important Reactions of Diolefins

Diolefins are hydrocarbons having two ethylene linkages in their molecular structure. Their empirical formula corresponds to C_nH_{2n-2}. For classification, diolefins may be divided into three types:

(1) The allenes, possessing the characteristic structure,

$$>C{=}C{=}C<$$

(2) The conjugated dienes (or butadiene type), with the structure,



$$>C{=}\overset{|}{C}{-}\overset{|}{C}{=}C<$$

(3) Other diolefins in which the double bonds are separated from one another by one or more CH_2 groups, among which may be specially mentioned the 1,4- and 1,5-dienes.

Of the three classes, the one emphasized in this chapter is the butadiene type which exhibits a high degree of reactivity and condensing power. The latter property is used to a great extent in the industrial separation of diolefins from the products of pyrolysis of petroleum hydrocarbons.[1]

It is significant to note the increasing number of important diolefin derivatives obtained from condensation reactions. For example, Horclois[2] prepared derivatives of cyclopentadiene from alkylated diethyl malonates. These were used as starting materials in the synthesis of many compounds which have application both as pharmaceuticals and in the perfume industry.

Interaction of conjugated diolefins with substances such as halogens, halogen acids and sulphur dioxide, reactions of 2-chlorobutadiene and some analytical procedures are included in this chapter. Most of the resultants, with the possible exception of chloroprene, may seem to be of academic interest since they have been applied industrially only to a limited extent. However, they should be considered as possible sources for future development of organic chemical synthesis.

PREPARATION OF DIOLEFINS

Conjugated diolefins, particularly butadiene and cyclopentadiene, are often found among the products of high-temperature pyrolysis of petroleum hydrocarbons.[3] Another source is from the thermal decomposition of alcohols. For example, by the passage of ethyl alcohol vapor over a mixed catalyst, Lebedev[4] obtained a 20 to 25 per cent yield of butadiene. The importance of temperature and contact time in this process has been investigated by Volzhinskii, Kogan and Neimark.[5] In general, their results indicate that the stability of the butadiene is decreased in the presence of the catalyst. For example, when a gas containing 11.14 per cent of butadiene was passed through a depth of 2 meters of catalyst at the rate of 14.5 cc. per second at 500°C., the proportion of diolefin was reduced to 7.51 per cent.

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[1] See Chapter 4.

[2] R. Horclois, *Chim. et ind.*, 1934, 31, 357; *Chem. Abs.*, 1935, 29, 140; *Brit. Chem. Abs.* B, 1934, 660.

[3] For a discussion of methods involving pyrolysis of hydrocarbons to diolefins, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. Also Chapter 4.

[4] S. V. Lebedev. *J. Gen. Chem.* (*U.S.S.R.*), 1933, 3, 698; *Brit. Chem. Abs.* A, 1934, 168; *Chem. Abs.*, 1934, 28, 3050. See also Chapter 4.

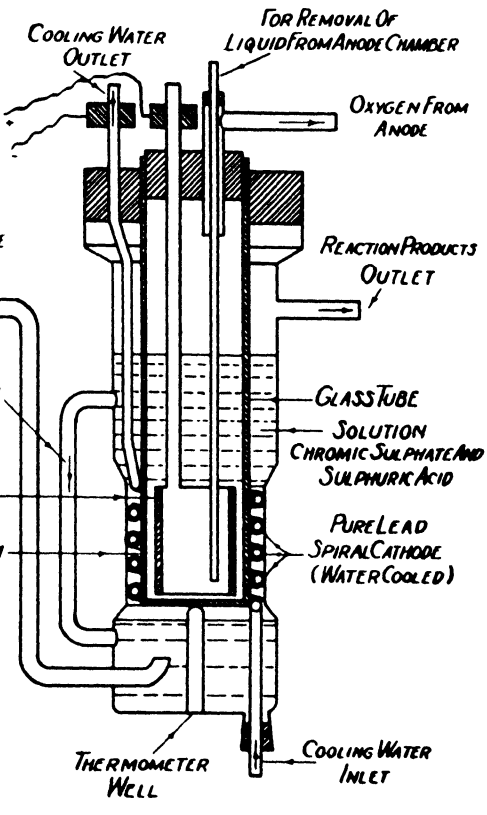


FIG. 151.—Sketch of Apparatus for Production of Butadiene. (P. Baumann and H. Tanneberger)

Diacetylene has been suggested by Baumann and Tanneberger[6] as a source of butadiene and they recommend the following procedure (See Fig. 151). In the reaction vessel is placed an aqueous solution which has the approximate composition: 11.6 per cent chromic sulphate, 5 per cent hydrogen sulphate and 83.4 per cent water. This solution is reduced electrolytically (using a cathode of pure lead), at a potential of about 5 volts and a current density of about 2.5 amperes per square decimeter of electrode surface. While this operation is being carried out at room temperature, or slightly above it, gaseous diacetylene (or a gaseous mixture

[5] I. A. Volzhinskii, G. M. Kogan and O. M. Neimark, *Sintet. Kauchuk*, 1936 (1), 4; *Chem. Abs.*, 1936, 30, 4147.

[6] P. Baumann and H. Tanneberger, U. S. P. 1,955,046, Apr. 17, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3744.

of essentially this substance) is slowly passed through the liquid. The exit gases are reported to contain a large percentage (60 per cent or more) of butadiene.

Preparation of butadiene has been effected by using *n*-butyl chloride as a raw material. The procedure involved, as described by Muskat,[7] consists in chlorinating 1-chlorobutane, the temperature initially being 77°C. but rising to about 115°C. at the end of the operation. A mixture of dichlorides thus formed and boiling between 77° and 160°C. was separated (by distillation) into six fractions. Each fraction was separately distilled and the vapors passed in a steel tube heated to about 700-730°C. and containing coarse soda lime. After this treatment, the vapors traveled in succession through cooling vessels to remove water, unreacted dichlorobutane and tarry and resinous products. The nearly pure butadiene formed in this manner was collected as the tetrabromide made by bubbling the diolefin through chloroform containing bromine. In Table 145, the yields from each fraction are given.

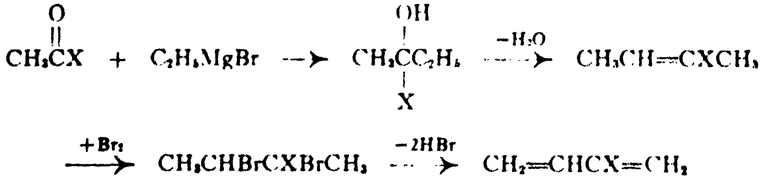
TABLE 145.—*Yields of Butadiene from Pyrolysis of Dichlorobutanes.*

Fraction Number	Boiling Range in °C.	Per cent Yield of Butadiene
1.	75-110	6.9
2.	110-120	18.8
3.	120-130	24.8
4.	130-140	29.6
5.	140-150	23.6
6.	150-165	25.6

In some instances homologues of this 1,3-diolefin may be obtained from derivatives of pinacone. For example, Backer and Strating[8] prepared 1,2,3,4-tetramethyl-1,3-butadiene in a 75 per cent yield by treating methylethylpinacone with hot 20 per cent sulphuric acid. This is represented as

$$\underset{\textit{methylethylpinacone}}{CH_3CH_2C(CH_3)(OH)C(CH_3)(OH)CH_2CH_3} \xrightarrow{-2H_2O} \underset{\textit{1,2,3,4-tetramethyl-1,3-butadiene}}{CH_3CH{=}C(CH_3)C(CH_3){=}CHCH_3}$$

Similarly, diethylpinacone, in the presence of alum at 140°C., was dehydrated to 1,4-dimethyl-2,3-diethyl-1,3-butadiene (b.p., 158-163°C.). The reactions by which two other compounds, 2-*ter*-butyl-1,3-butadiene (b.p., 104-106°C.) and 2-phenyl-1,3-butadiene (b.p. 58-59°C. at 9 mm.) were obtained, were also carried out by these workers. In both instances the starting material (a ketone) was treated with ethyl magnesium bromide and the resulting product was subsequently distilled in the presence of sulphuric acid. Bromination followed by another distillation under 25 millimeters pressure yielded the corresponding conjugated diene. This series of transformations is indicated below for the two examples mentioned. The symbol *X* represents either the *ter*-butyl or phenyl group.



$$CH_3\overset{\overset{O}{\|}}{C}X + C_2H_5MgBr \longrightarrow CH_3\overset{\overset{OH}{|}}{\underset{\underset{X}{|}}{C}}C_2H_5 \xrightarrow{-H_2O} CH_3CH{=}CXCH_3$$

$$\xrightarrow{+Br_2} CH_3CHBrCXBrCH_3 \xrightarrow{-2HBr} CH_2{=}CHCX{=}CH_2$$

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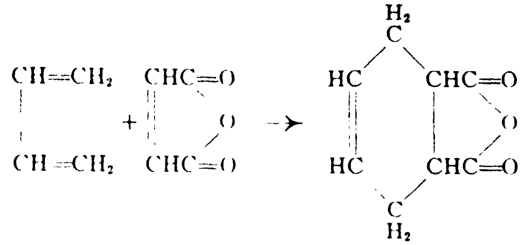
[7] I. E. Muskat, U. S. P. 2,038,593, Apr. 28, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 3912.

[8] H. J. Backer and J. Strating, *Rec. trav. chim.*, 1934, **53**, 525; 1935, **54**, 170; *Brit. Chem. Abs.* **A**, 1934, 662; 1935, 497; *Chem. Abs.*, 1934, **28**, 4697; 1935, **29**, 2959.

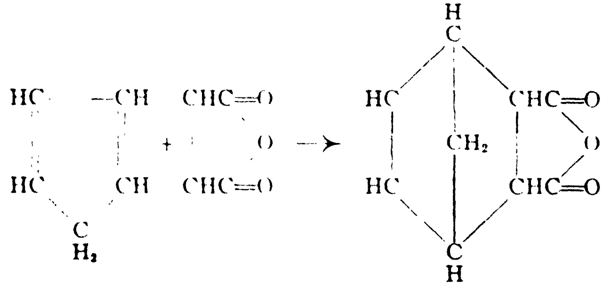
A small yield of 2,3-di-*ter*-butyl-1,3-butadiene was also secured by dehydrating 3-hydroxy-3,4-di-*ter*-butyl-1-butene with hot oxalic acid.

Horclois[9] reported that cyclopentadiene is obtained in the form of crystalline dicyclopentadiene as a by-product from coke oven gases. The rate of recovery is about 15 to 20 kilograms per 1000 tons of coal. As previously mentioned, certain derivatives of this cyclic 1,3-diolefin are applicable in the pharmaceutical and perfumery industries.

The separation of conjugated diolefins from crude benzol, or other liquid hydrocarbons, by interaction with maleic anhydride is described by Krzikalla and Wolff.[10] It is pointed out that by adding the anhydride in small portions and separating the resulting product after each addition, isolation of individual diolefins may be effected.[11] For butadiene the reaction can be represented as



and for cyclopentadiene as



In some instances, particularly with the latter diolefin and its homologues, *p*-quinones may be substituted for maleic anhydride.[12]

Reaction with quinones may be regulated so as to secure a separation of the diolefins. For example, Stern and Hoess[12a] suggest treatment of 1000 parts of cracked petroleum distillate (boiling up to 150°C.) with 70 parts of α-naphthoquinone. The liquid mass is then subjected to distillation (under reduced pressure), and the addition product of methylcyclopentadiene and α-naphthoquinone is secured as a residue. Interaction of the liquid with another portion (15 parts) of the quinone, followed by distillation, furnished a mixture of methylcyclopentadiene and cyclopentadiene adducts. Furthermore, another treatment with α-naphthoquinone (25 parts) and distilling yielded a residue of the addition product with cyclopentadiene.

[9] R. Horclois, *Chim. et ind.*, 1934, **31**, 357 (special number); *Chem. Abs.*, 1935, **29**, 140; *Brit. Chem. Abs.* **B**, 1934, 660.

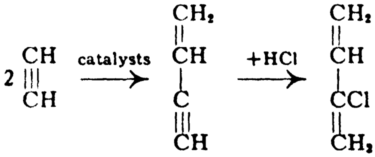
[10] H. Krzikalla and W. Wolff, German P. 583,536, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1046. For a discussion of this reaction, also known as the "Diene Synthesis," see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[11] British P. 438,810, 1935, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1936, 137; *Chem. Abs.*, 1936, **30**, 3220; *J. Inst. Pet. Tech.*, 1936, **22**, 55A. French P. 785,852, 1935; *Chem. Abs.*, 1936, **30**, 1383.

[12] French P. 785,851, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 1383.

[12a] G. Stern and W. Hoess, U. S. P. 2,067,511, Jan. 12, 1937, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, **31**, 1429.

2-Chlorobutadiene. The industrial preparation of 2-chlorobutadiene is effected mainly by two reactions.[13] First, acetylene is polymerized in the presence of catalysts to form monovinylacetylene; and second, the latter hydrocarbon is treated with hydrogen chloride. These may be represented as follows:



$$2\,\begin{matrix}CH\\|||\\CH\end{matrix} \xrightarrow{\text{catalysts}} \begin{matrix}CH_2\\||\\CH\\|\\C\\|||\\CH\end{matrix} \xrightarrow{+HCl} \begin{matrix}CH_2\\||\\CH\\|\\CCl\\||\\CH_2\end{matrix}$$

acetylene *monovinylacetylene* *2-chloro-1,3-butadiene*
(chloroprene)

The presence of certain agents, especially cuprous chloride, causes an almost quantitative yield of this chlorolefin, or chloroprene, to be obtained in the second reaction. However, Nieuwland[14] pointed out that 2-chlorobutadiene is formed through an intermediate step. That is, a 1,4-addition of hydrogen chloride first takes place, and the resulting compound (chloromethylallene) then isomerizes to chloroprene under the influence of cuprous chloride.

$$CH_2{=}CH{-}C{\equiv}CH + HCl \rightarrow CH_2(Cl){-}CH{=}C{=}CH_2 \rightarrow CH_2{=}C(Cl){-}CH{=}CH_2$$

Another procedure comprises passage of vinylacetylene mixed with hydrogen chloride over activated charcoal.[14a] The latter may be coated with metallic chlorides, those of the heavier metals of Groups 2 and 4 of the Periodic System.

Using acetaldehyde and acetylene as starting materials, Carothers and Coffman[15] also synthesized 2-chlorobutadiene. In that method, a mixture of acetaldehyde and ether, at about —10°C., was treated for 8 hours with powdered sodamide and acetylene under superatmospheric pressure. The methylethinylcarbinol formed was purified and then dehydrated in the vapor phase by passage over basic aluminum sulphate at 240-260°C. Monovinylacetylene obtained in this way was freed of unchanged alcohol by fractional distillation. This was followed by cooling the hydrocarbon and reacting it with a thoroughly chilled mixture of hydrochloric acid, cuprous chloride and ammonium chloride in an autoclave. The product, after being held at 30°C. for 4 hours, yielded on steam distillation, from 75 to 92 per cent of chloroprene. The different steps in this operation may be represented by:

$$\underset{\textit{acetaldehyde}}{O{=}CHCH_3} + \underset{\textit{acetylene}}{HC{\equiv}CH} \longrightarrow \underset{\textit{methylethinylcarbinol}}{HC{\equiv}C{-}CHOHCH_3}$$

$$\xrightarrow{-H_2O} \underset{\textit{monovinylacetylene}}{HC{\equiv}C{-}CH{=}CH_2} \xrightarrow{+HCl} \underset{\textit{2-chloro-1,3-butadiene}}{CH_2{=}CClCH{=}CH_2}$$

Another method of preparation has been developed by Carothers.[16] 3,4-Dichloro-1-butene is caused to react with an amount of alkali (such as potassium hydroxide) which will remove half of the chlorine as hydrogen chloride, according to the following equation:

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[13] See Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935, 154, and Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934, 638, 669.

[14] J. A. Nieuwland, *Ind. Eng. Chem.*, 1935, 27, 850; *Chem. Abs.*, 1935, 29, 4981. See also W. H. Carothers and A. M. Collins, U. S. P. 1,950,431, Mar. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3271.

[14a] British P. 458,100, 1936, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech.*, 1937, 31, 79A.

[15] W. H. Carothers and D. D. Coffman, U. S. P. 1,950,441, Mar. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3270.

[16] W. H. Carothers, U. S. P. 2,038,538, Apr. 28, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, 30, 3838.

$$CH_2{=}CHCHClCH_2Cl \xrightarrow{+KOH} CH_2{=}CHCCl{=}CH_2$$

By fractional distillation, the product can be separated from any unreacted material. Carothers stated that 2-bromo-1,3-butadiene may be obtained in a similar manner.

Chloroprene is a colorless liquid which boils at 59.4°C. under atmospheric pressure and has a specific gravity of 0.9583 at 20°C. It undergoes polymerization to yield at least four distinct substances.[17] Of the latter, two types designated as α- and μ-polymers are the most important. The former is a soft, plastic body which is soluble in benzene, and has been marketed under the name of Duprene.[18] It may be separated from admixed polymers by precipitation with alcohol. The μ-variety resembles vulcanized rubber in physical properties, and is non-plastic and elastic.

In order to isolate the α-polyprene, Williams[19] has proposed two methods to effect separation of this polymer. First, when the polymerization mixture is of thick consistency (e.g., glycerol) or almost too thick to pour, a selective solvent is added. Such a compound dissolves the unreacted material and leaves free the soft rubbery mass. Further treatment with fresh solvent, followed by squeezing in a roll and heating to drive out last traces of the liquid are the subsequent steps used in this first process. Among the solvents that may be employed are methyl, ethyl, propyl, isopropyl and butyl alcohols, acetone, methyl ethyl ketone and diethyl ketone. The second method consists in distilling off the unchanged chloroprene under reduced pressure when polymerization has proceeded to the same extent as in the first procedure. Pressures recommended are from 6 cm. of mercury to atmospheric pressure and temperatures of from 25 to 70°C. A flexible, oil-resistant rubber composition of considerable tensile strength has been prepared from the benzene-soluble, alcohol-insoluble product of the complete or partial polymerization of chloroprene.[20]

Polymerization can be controlled by the use of added inhibitors such as a phenol, quinone, amine, nitro aryl compounds, ethyl selenide, iodine, bromine, certain sulphur-bearing organic compounds,[21] sulphur or thiuram disulphide.[22] The polymers are said to be more plastic at atmospheric temperatures when incorporated with 4 to 10 per cent of a ketone, for example, camphor, acetophenone, benzophenone or fenchone.[22a] Co-polymerization of chloroprene may be effected in the presence of diolefins such as 2,3-dimethylbutadiene,[22b] vinyl compounds,[23] e.g., ethers, esters, or carbinol derivatives, or α,β-unsaturated aldehydes, ketones, acids, esters, anhydrides or nitriles.[23a] Carothers[23b] advocates chlorination of polymeric 2-chlorobutadiene to secure rubber-like materials exhibiting flexibility even after long periods of storage or subjection to low temperatures. One method of treatment comprises dissolving the polymerized chlorohydrocarbon (30 parts) in chloroform (250 parts) and conducting a rapid stream of chlorine for 1.5 hours into the solution maintained at a temperature of 45°C. and out of contact with sunlight. Afterwards the liquid mass is kept at 20°C. for 16 hours. The solvent may then be removed by evaporation or the solid product precipitated by the addition of alcohol.

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[17] For a discussion of the polymerization of chloroprene, see, Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[18] Duprene is also known as Neoprene (see *Ind. Eng. Chem., News Ed.*, 1937, **15**, 43). The latter term has been suggested for use in a general sense, that is, it can designate the crude material or the products manufactured from it. In U.S.S.R., chloroprene synthetic rubber is referred to as Sovprene. Consult A. L. Klebanskii, L. G. Tzyurikh and I. M. Dolgopol'skii, *Bull. acad. sci. U.R.S.S.*, **1935** (2), 189; *J. Research Assoc. Brit. Rubber Mfrs.*, 1935, **4**, 505; *Rubber Chem. Tech.*, 1936, **9**, 383; *Chem. Abs.*, 1936, **30**, 7908. For a discussion of the toxicity of crude Duprene, see W. F. v. Oettinger and W. Deichmann-Gruebler, *J. Ind. Hyg. Toxicol.*, 1936, **18**, 271; *Chem. Abs.*, 1936, **30**, 3881; *Brit. Chem. Abs.* **A**, 1936, 758.

[19] I. Williams, U. S. P. 1,950,436, Mar. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 3271.

[20] M. Jones and W. F. Smith, British P. 428,052, 1935, to Imperial Chemical Industries Ltd.; *Brit. Chem. Abs.* **B**, 1935, 644; *Chem. Abs.*, 1935, **29**, 6800; *J. Inst. Pet. Tech.*, 1935, **21**, 309A.

[21] W. H. Carothers, A. M. Collins and J. E. Kirby, U. S. P. 1,950,438, Mar. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 3271.

[22] W. H. Carothers and J. E. Kirby, U. S. P., 1,950,439, Mar. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 3271.

[22a] French P. 799,345, 1936, to United States Rubber Co.; *Chem. Abs.*, 1936, **30**, 7911. British P. 452,078, 1935; *Brit. Chem. Abs.* **B**, 1936, 1009.

Courtesy Chemical and Metallurgical Engineering
Courtesy E. I. du Pont de Nemours & Co.

FIG. 152.—Intermediate Stage in Processing Neoprene, a Chloroprene Rubber.

The decomposition of chloroprene polymers resulting in the elimination of hydrogen chloride has been inhibited by derivatives of ethylene oxide of high boiling point, such as alkyl or aryl ethers of glycidic acid and its esters, added to the extent of 0.5 to 4 per cent.[23c]

[22b] W. H. Carothers, A. M. Collins and J. E. Kirby, U. S. P. 2,066,329, Jan. 5, 1937, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, **31**, 1250.

[23] W. H. Carothers, A. M. Collins and J. E. Kirby, U. S. P. 2,066,330, Jan. 5, 1937, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, **31**, 1250.

[23a] W. H. Carothers, A. M. Collins and J. E. Kirby, U. S. P. 2,066,331, Jan. 5, 1937, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, **31**, 1250.

[23b] W. H. Carothers, U. S. P. 2,067,172, Jan. 12, 1937, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, **31**, 1432.

[23c] British P. 440,957, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 4175; *Brit. Chem. Abs.* **B**, 1936, 264; *J. Inst. Pet. Tech.*, 1936, **22**, 263A. For a discussion of the possibilities of synthetic rubber from butadiene alkoxy derivatives see I. A. Rotenberg and M. A. Favorskaya, *J. Gen. Chem. (U.S.S.R.)*, 1936, **6**, 185; *Brit. Chem. Abs.* **A**, 1936, 964; *Chem. Abs.*, 1936, **30**, 4808.

Halogen Derivatives of Conjugated Diolefins

Addition of Bromine. Observations on the addition of halogens to most conjugated dienes indicate that the 1,4 compound is formed in the greatest amount.[24] From a theoretical standpoint, Eyring, Sherman and Kimball[25] arrived at this conclusion in the case of the addition of bromine to butadiene, the equation for which is given as follows:

$$CH_2{=}CHCH{=}CH_2 + Br_2 \longrightarrow CH_2BrCH{=}CHCH_2Br$$

They also stated that the reaction would be catalyzed by the walls of the container. Heisig and Wilson[26] made a kinetic study of this reaction carried out in various-sized spheres on glass and paraffined surfaces. The velocity constants were calculated, assuming that the reaction was bimolecular and that the reactants were weakly absorbed, using the formula

$$k = \frac{x}{at\,(a - x)}$$

where a is the initial partial pressure of bromine and butadiene (equal in this reaction) and x is the decrease in the pressure at the time t.

These investigators observed that the rate of reaction increased, in general, until a sufficient quantity of the product (1,4-dibromobutene) formed to saturate the gases with its vapor and also coat the walls of the spheres with a unimolecular layer. After that time the rate became constant. This phenomenon was not so apparent in large containers as in small ones. Some typical data obtained after the reacting gases were saturated with the dibromobutene are given in Table 146.

TABLE 146.—k × 10^2 *For Reaction between Butadiene and Bromine after the Gases are Saturated with Product in Medium Sized Spheres.*

	Uncoated Vol., 275.4 cc; diam., 8.1 cm. a = b = 13.2		Paraffined net vol., 274 cc. a = b = 13.2		Beads net vol., 122.1 cc. a = b = 5	
t, min.	$-\Delta P$	k	$-\Delta P$	k	$-\Delta P$	k
1	8.9	4.5	6.1	2.8	6.3	34
2	12.3	3.5	10.5	2.5	8.3	42
3	14.9	3.3	14.0	2.9	8.6	41
4			16.2	3.0	8.8	37
5	18.7	3.7	17.8	3.1	8.9	32
6	19.5	3.6	19.1	3.3		
7	20.1	4.3	20.3	3.6	9.0	26
8	20.5	3.3	21.1	3.8	9.1	25
9.	21.3	3.5	21.8	4.0		
10	21.4	3.3	22.3	4.1		
12. . .	22.1	3.2	23.1	4.4	9.3	22
14. . . .	22.6	3.2				
16. . . .	23.1	3.3				
∞.	17.4		26.2		10.0	
av. for. . . .	72%	3.5	81%	3.1	93%	37

The increased reaction velocity with increase in surface is clearly shown in the case of the spherical containers packed with glass beads.

The product of the velocity constant k and the sphere diameter d was also found to be constant, and was considered as evidence for a surface reaction. Another conclusion drawn from the constancy of the product *kd* was "the reaction must occur on a surface of reaction product rather than the wall itself." Some values of *kd* are shown in Table 147. In each instance equimolecular volumes of butadiene and bromine were employed.

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[24] For a discussion of this subject see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[25] H. Eyring, A. Sherman and G. E. Kimball, *J. Chem. Physics*, 1933, 1, 586; *Brit. Chem. Abs.* A, 1934, 35; *Chem. Abs.*, 1933, 27, 5594.

[26] G. B. Heisig and J. L. Wilson, *J.A.C.S.*, 1935, 57, 859; *Chem. Abs.*, 1935, 29, 4248; *Brit. Chem. Abs.* A, 1935, 827; *J. Inst. Pet. Tech.*, 1935, 21, 255A.

TABLE 147.—*Values of* kd ($\times 10^2$) *for Experiments in which Butadiene and Bromine Reacted on Surface of Product.*

	Uncoated			Paraffined		
Diameter of Sphere	4.6 cm.	8.1 cm.	10.0 cm.	4.6 cm.	8.1 cm.	10.0 cm.
k	6.3	3.8	3	5.5	3.8	2.9
kd	29	30	30	25.3	30	29

The bromination of cyclopentadiene has been shown to be incomplete when conducted in air, due to the absorption of oxygen.[27] The observation led Heisig and Davis[28] to study the effect of oxygen on the reaction between bromine and butadiene. They found that the rate of reaction increased with the decrease of oxygen present, and that the increase was especially noticeable when the partial pressure of the oxygen was well below 2 mm. This is illustrated by data in Table 148. In all instances the course of combination of gaseous olefin and halogen was measured by the decrease in pressure (in mm. of α-bromonaphthalene, the manometer fluid) within the reaction vessel.

TABLE 148.—***Reaction between Bromine and Butadiene with Various Concentrations of Oxygen.***

Time		Press. of Oxygen, mm.			
		375	2	Small Trace	0
Min.	Sec.	Pressure Drop, mm. of α-Bromonaphthalene			
0	5	1.8	3.5	7.8	12.0
	10	3.5	6.2	11.4	15.0
	20	6.6	9.9	14.6	18.0
	30	9.3	12.4	16.7	19.8
	40	11.4	14.3	18.1	20.9
	50	12.9	15.8	18.8	21.6
1	0	14.2	17.1	19.4	22.1
1	30	16.8	20.1	20.6	22.8
2		18.6	21.9	21.4	23.3
2	30	19.8	23.1	21.9	23.5
3		20.8	24.0	22.2	23.7
4		21.9	25.2	22.6	23.9
5		22.9	25.9	22.8	24.5
7		24.1	26.8	22.9	24.6
10		25.0	27.3	23.3	24.7
15		26.0	27.9	23.6	25.0
20		26.2	28.3	23.9	25.3
30		27	28.6	24.4	25.7
∞		28.7	29.6	25.3	27.0

On the basis of their data, the conclusion was made that transformation first took place mainly at the surface of the container. The sensitivity of the rate of reaction to oxygen suggests a chain mechanism with short chains begun at that surface.

Bromination of butadiene was employed by Tzyurikh and Rotenberg[29] in the synthesis of 1,4-dibromobutane. The resulting mixture of stereoisomeric 1,4-dibromo-2-butenes was converted to 1,4-diethoxy-2-butene by wetting with a little alcohol and gradually mixing with a calculated amount of sodium ethylate. The ether thus formed was hydrogenated at room temperature in alcohol using palladium and nickel catalysts, and yielded 1,4-diethoxybutane. The latter was heated in a sealed tube with concentrated hydrogen bromide at 130°C. for 3 hours to give 1,4-dibromobutane. This series of reactions is outlined in the following scheme.

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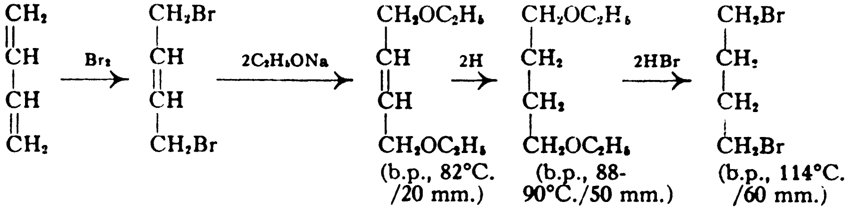
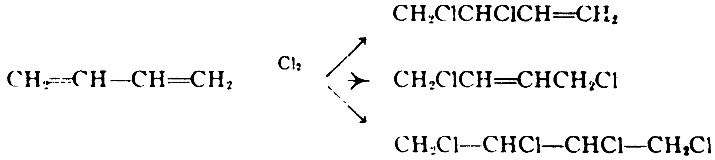
[27] G. R. Schultze, *J.A.C.S.*, 1934, **56**, 1552; *Chem. Abs.*, 1934, **28**, 5047; *Brit. Chem. Abs.* **A**, 1934, 995. Cf. section in this chapter on analytical reactions.

[28] G. B. Heisig and H. M. Davis, *J.A.C.S.*, 1936, **58**, 1095; *Chem. Abs.*, 1936, **30**, 6272; *Brit. Chem. Abs.* **A**, 1936, 1090; *J. Inst. Pet. Tech.*, 1936, **22**, 436A.

[29] L. G. Tzyurikh and I. A. Rotenberg, *J. Gen. Chem.* (*U.S.S.R.*), 1936, **6**, 203; *Brit. Chem. Abs.* **A**, 1936, 962; *Chem. Abs.*, 1936, **30**, 4809.



Addition of Chlorine. Interaction of chlorine and butadiene furnishes a mixture of 1,2- and 1,4-dichlorobutenes, of which the latter is formed in the greater proportion. At the same time some tetrachlorobutadiene (both *cis* and *trans* forms) is produced.[30] These reactions can be represented by:



In the preparation of these compounds, Muskat[31] suggests that the gaseous diolefin and halogen be passed simultaneously into a liquid medium (e.g., carbon disulphide) cooled by an ice-salt bath. The resulting mixture of chlorinated compounds may be separated afterwards by fractional distillation. He also points out that both 1,2- and 1,4-dichloro compounds polymerize when subjected to the action of alkaline (for example, sodium hydroxide, soda-lime, or ammonia) or acidic (such as sulphuric acid, zinc chloride or boron trifluoride) condensing agents. These polymers are brown, solid resins.

When 1,4-dichlorobutene-2, mixed with twice its weight of powdered potassium hydroxide, is heated to about 90°C., dechlorination occurs with the formation chloro-1-butadiene-1,3.

$$CH_2ClCH=CHCH_2Cl \longrightarrow CHCl=CH-CH=CH_2 + HCl$$

This is a colorless liquid boiling at 67-68°C., has a density of about 0.958 (at 20°C.) and a refractive index (n_D^{20}) of 1.470. On standing, it polymerizes spontaneously to a colorless resin.

According to Muskat, dechlorination (as described above) of the mixed dichlorobutenes furnishes chloro-1-butadiene-1,3, monovinylacetylene, an acetylenic hydrocarbon (of undetermined structure), and a resinous body (as a residue). The first three may be separated by fractional distillation, and each subjected to polymerization to give almost colorless resins. Co-polymerization of the two acetylene derivatives admixed with 1-chlorobutadiene may be effected also. The recommended mode of operation is application of pressure to the compounds in the presence of air and with exposure to light.

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[30] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[31] I. E. Muskat, U. S. P. 2,038,593, Apr. 28, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 3912.

Chlorination of isoprene has been investigated by Jones and Williams.[32] These workers added a carbon tetrachloride solution of chlorine to a solution of isoprene in the same solvent over a period of 4 hours, the mixture being mechanically stirred and cooled by an ice-salt bath. The resulting composite was fractionated and the substances obtained are listed in Table 149.

TABLE 149.—*Chlorination Products of Isoprene.*

Substance Obtained	Formula	B.p. °C.	Press. mm.	% of total
1-Chloro-2-methyl-1,3-butadiene	$CHCl{=}CCH_3CH{=}CH_2$	50.4	100	38
1,4-Dichloro-2-methyl-2-butene.	$CH_2ClCCH_3{=}CHCH_2Cl$	93	50	45
A lower boiling dichloride......	—	60	50	6
Undistillable residue...........	—	—	—	11

Addition of Halogen Acids. As in the case of bromine, the presence of oxygen affects the addition of hydrogen bromide to butadiene. Kharasch, Margolis and Mayo[33] found that a yield of 70 to 90 per cent of 1-bromo-2-butene was obtained in air and also in the presence of added peroxides. But, in the absence of oxygen and in the presence of antioxidants, hydrogen bromide combines with butadiene to give 2-bromo-2-butene in 65 to 90 per cent yields. These workers suggested that 1-bromo-2-butene could have been formed either by direct 1,4 addition or by a rearrangement of the 2-bromo-2-butene under the influence of hydrogen bromide alone or with peroxides. Ganguly[33a] reports that interaction of hydrogen chloride and butadiene furnishes the two isomers $CH_3CHClCH{=}CH_2$ and $CH_3CH{=}CHCH_2Cl$. The third isomer, $CH_2ClCH_2CH{=}CH_2$, was not detected.

Combination of halogen acids and 1,3-dienes generally takes place in the 1,4 position. However, there are exceptions, as in the reaction just mentioned. In another example, negative group substitutions in butadiene (in the cases of 1-phenylbutadiene and 1-bromobutadiene) have been noted to result in a 3,4 addition of hydrogen bromide. Muskat and Huggins[34] showed that hydrogen chloride reacts with the geometric isomers of 1-phenylbutadiene to form the *cis-* and *trans-*1-phenyl-3-chloro-1-butene, which boil at 106°C. (at 5 mm.) and 103°C. (at 5 mm.), respectively. Their structures were determined by ozonization to be the result of absorption in the 3,4 positions. That these compounds were 3-chloro derivatives was shown by identifying the hydroxy derivative of the *cis* isomer and comparing the *trans* isomer with the hydrogen chloride addition product of *trans-*1-phenyl-3-hydroxy-1-butene.

The action of dry hydrogen chloride under pressures of about 10 atmospheres on butadiene compounds and their polymers results in a material which is spongy and asbestos-like in texture. The time of reaction is about 8 hours and can be decreased by using catalysts as, e.g., aluminum chloride. The product thus formed, after removal of excess hydrogen chloride, is relatively stable at 100°C. and may be used in the manufacture of transparent films.[35]

Substituted Derivatives. The preparation of 2,3-dichlorobutadiene has been described by Carothers and Berchet.[36] In that process, 1,2,3,4-tetrachlorobutane is treated with a 30 per cent methyl alcohol solution of potassium hydroxide or with solid sodium hydroxide at 10° to 18°C. The reaction in this instance is:

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[32] W. J. Jones and H. G. Williams, *J.C.S.*, 1934, 829; *Chem. Abs.*, 1934, **28**, 5399; *Brit. Chem. Abs.* **A**, 1934, 864.

[33] M. S. Kharasch, E. T. Margolis and F. R. Mayo, *Chemistry and Industry*, 1936, 663; *Chem. Abs.*, 1936, **30**, 8144. *J. Org. Chem.* 1936, 1, 393; *Chem. Abs.*, 1937, **31**, 1758. For the effect of peroxides on the addition of halogen acids to monolefins, see Chapter 12

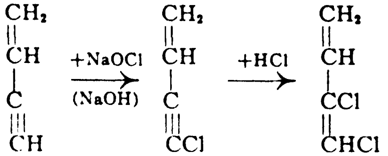
[33a] S. N. Ganguly, *J. Indian Chem. Soc.*, 1936, **13**, 580; *Chem. Abs.*, 1937, **31**, 1758.

[34] I. E. Muskat and K. A. Huggins, *J.A.C.S.*, 1934, **56**, 1239; *Chem. Abs.*, 1934, **28**, 4390; *Brit. Chem. Abs.* **A**, 1934, 762.

[35] British P. 447,110, 1936, to Marsene Corporation of America; *Brit. Chem. Abs.* **B**, 1936, 752; *J. Inst. Pet. Tech.*, 1936, **22**, 297A.

$$CH_2Cl{-}CHCl{-}CHCl{-}CH_2Cl \xrightarrow{+2KOH} CH_2{=}CCl{-}CCl{=}CH_2 + 2KCl + 2H_2O$$

The synthesis of 1,2-dichlorobutadiene has been reported,[37] and is briefly as follows: monovinylacetylene is shaken for 16 hours with aqueous sodium hypochlorite containing 15 per cent of sodium hydroxide. This is followed by treatment for 16 hours with fuming hydrochloric acid (acid of sp. gr. 1.19 in which about 50 per cent more hydrogen chloride has been dissolved), cuprous chloride and ammonium chloride. The two steps may be summarized as follows:

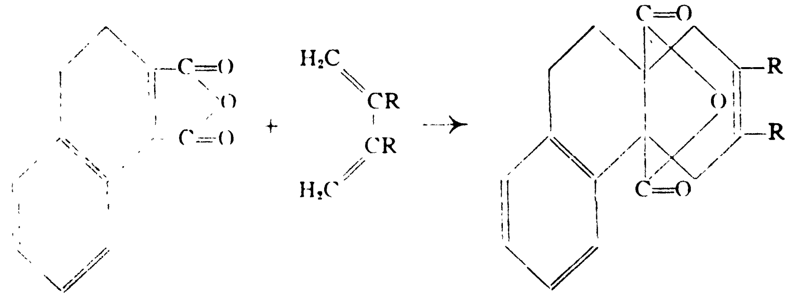


$$CH_2{=}CH{-}C{\equiv}CH \xrightarrow[(NaOH)]{+NaOCl} CH_2{=}CH{-}C{\equiv}CCl \xrightarrow{+HCl} CH_2{=}CH{-}CCl{=}CHCl$$

The product has a boiling point of 60-65°C. at 105 mm., and can be polymerized spontaneously to a rubbery substance which may be vulcanized to an ebonite-like material.

CONDENSATION REACTIONS OF CONJUGATED DIOLEFINS

Butadiene enters into direct combination with many aromatic compounds. Fieser and Hershberg[38] state that the following reaction is of general application to synthesis:



where *R* is an alkyl group or hydrogen. For example, these investigators prepared 1,4,9,10,11,12-hexahydrophenanthrene-11,12-dicarboxylic acid anhydride (b.p., 160-170°C.) in a 63 per cent yield by heating butadiene with 3,4-dihydronaphthalene-1,2-dicarboxylic acid anhydride for 85 hours at 100°C. Using 2,3-dimethyl-1,3-butadiene, the compound 2,3-dimethyl-1,4,9,10,11,12-hexahydrophenanthrene-11,12-dicarboxylic acid anhydride was also obtained. Other compounds prepared were 2,3-dimethyl-1,4,11,12,13,14-hexahydrochrysene-13,14-dicarboxylic acid anhydride

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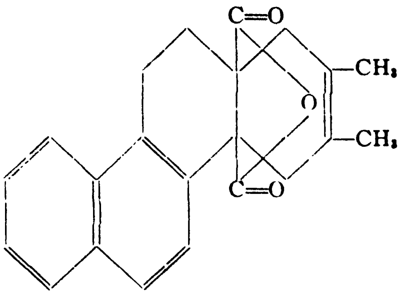
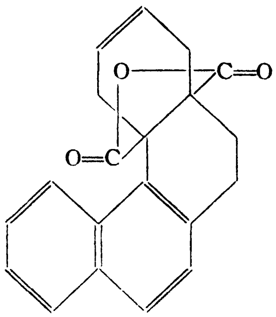
[36] W. H. Carothers and G. J. Berchet, U. S. P. 1,998,442, Apr. 23, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 3692; *Brit. Chem. Abs.* **B**, 1936, 487.

[37] A. L. Klebanskii, A. S. Volkenshtein and A. P. Orlova, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 1255; *J. prakt. Chem.*, 1936, **145**, 1; *Chem. Abs.*, 1936, **30**, 1025, 4147; *Brit. Chem. Abs.*, **A**, 1936, 187.

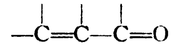
[38] L. F. Fieser and E. B. Hershberg, *J.A.C.S.*, 1935, **57**, 2192; *Chem. Abs.*, 1936, **30**, 95; *Brit. Chem. Abs.* **A**, 1936, 203.



and 5,6-benz-1,4,9,10,11,12-hexahydrophenanthrene-11,12-dicarboxylic acid anhydride



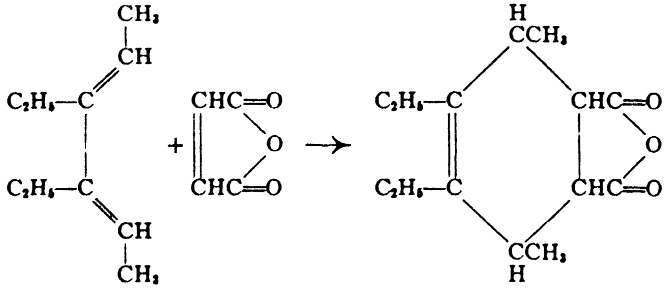
The condensations mentioned above involve a system of conjugated double bonds, found in the butadiene type of diolefins, reacting with the grouping



$$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O$$

Diels and Alder[39] include in this class of reactants quinones, maleic acid, maleic anhydride, itaconic anhydride and citraconic anhydride which easily form condensation products with conjugated diolefins as butadiene, cyclopentadiene and phellandrene. Among the many addition compounds thus prepared were terpenes, sesquiterpenes, alkaloids, camphors and hydrogenated cyclic compounds.

A further example is the interaction between maleic anhydride and 1,4-dimethyl 2,3-diethylbutadiene (b.p., 158-163°C.) to form 1,4-dimethyl-2,3-diethyl-1,4,5,6-tetrahydro-phthalic anhydride.[40]



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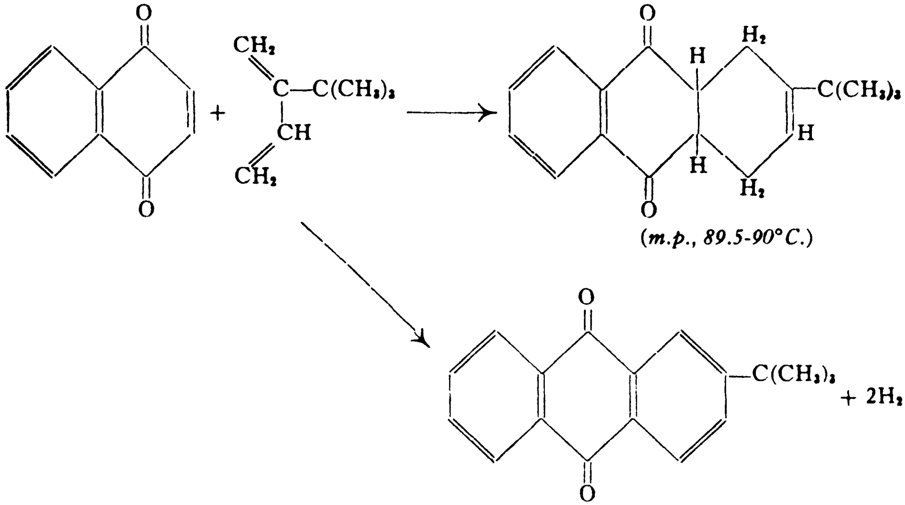
[39] O. Diels and K. Alder. U. S. P. 1.944,731, Jan. 23, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 2016. See also Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935, Chapter 40 for a discussion of the "Diene Synthesis."

[40] H. J. Backer and J. Strating, *Rec. trav. chim.*, 1934, **53**, 525; 1935, **54**, 170; *Brit. Chem. Abs.* **A**, 1934, 662; 1935, 497; *Chem. Abs.*, 1934, **28**, 4697; 1935, **29**, 2959.

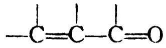
The use of quinones in place of acid anhydrides is illustrated by the union of 2-*ter*-butylbutadiene (b.p., 104-106°C.) and naphthaquinone to yield 2-*ter*-butylanthraquinone and 2-*ter*-butyl-1,4,13,14-tetrahydroanthraquinone.[41] This may be expressed as follows:



(*m.p., 89.5-90°C.*)

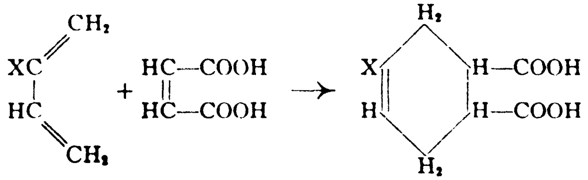
(*m.p., 104-105°C.*)

According to Carothers and Collins,[42] cyclic derivatives may be prepared by condensing 2-substituted 1,3-dienes with compounds containing a system of double bonds, many of which have the afore-mentioned structure

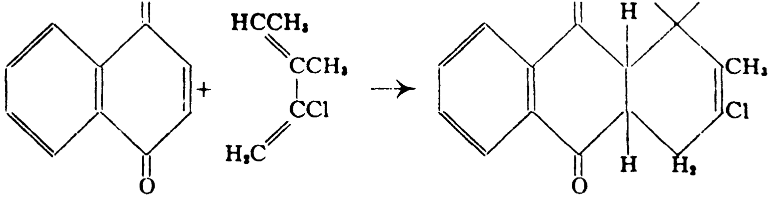


$-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O$

The following are two examples of this type of reaction.



X = Cl or Br



1,4-naphthaquinone *3-chloro-1,2-dimethylbutadiene* *3-chloro-1,2-dimethyl-1,4,4a,9a-tetrahydroanthraquinone* (m.p., 107°C.)

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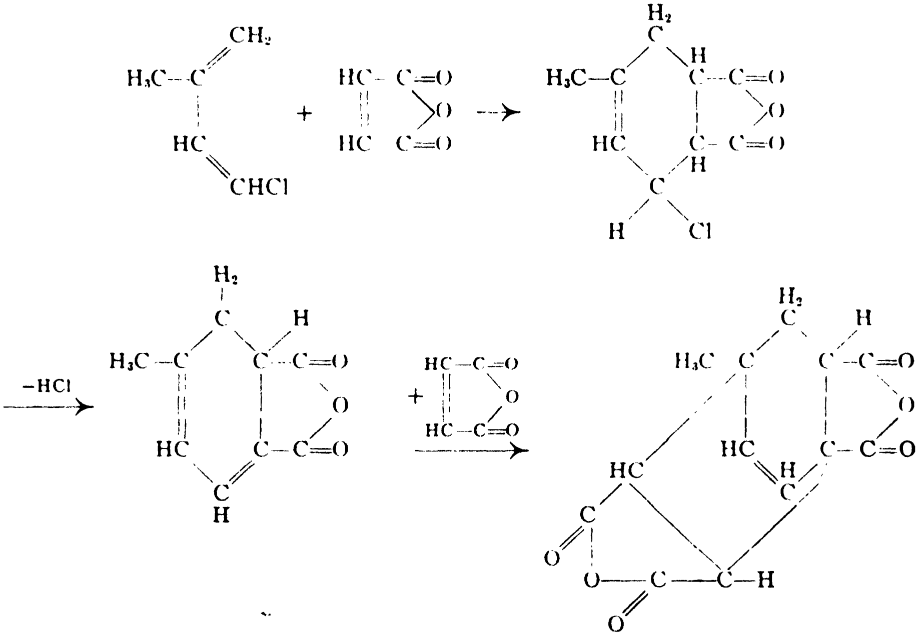
[41] H. J. Backer and J. Strating, *loc. cit.*

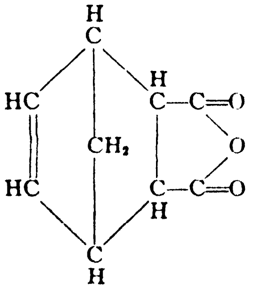
[42] W. H. Carothers and A. Collins, U. S. P. 1,967,862, July 24, 1934, to E. I. du Pont de Nemours & Co., *Chem. Abs.*, 1934, 28, 5994; *Brit. Chem. Abs.* B, 1935, 621.

These workers obtained intermediates of dyes, perfumes and medicinal compounds by analogous procedures.

An unusual condensation of 2-methyl-4-chlorobutadiene with maleic anhydride was observed by Favorskii and Favorskaya,[43] in which the transformation was accompanied by a vigorous evolution of hydrogen chloride gas. They believed that the following represents the course of the reaction finally resulting in a tetracarboxylic acid (or its anhydride).



It is interesting to note that methylene tetrahydrophthalic acid anhydride has



(m.p., 162° C.)

been isolated from the products obtained by treatment of crude benzol (from coke ovens and gas plants) with maleic anhydride.[44]

Isoprene has been found to condense with acrolein or acrylic acid, both of which contain a system of conjugated double bonds.[45] For instance, acrylic acid reacts with isoprene at about 110°C. in an autoclave to give 4-methyl-1,2,3,6-tetrahydrobenzoic acid. The reaction may be represented as follows:

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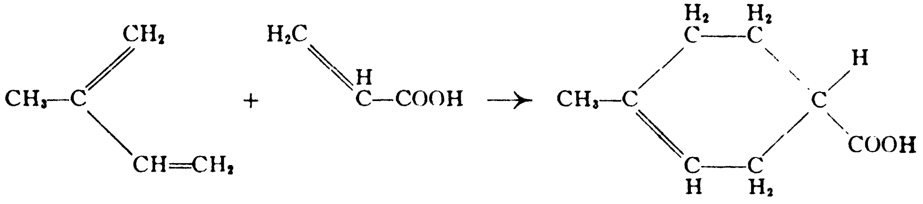
[43] A. Favorskii and T. Favorskaya, *Compt. rend.*, 1935, **200**, 839; *Chem. Abs.*, 1935, **29**, 3651; *Brit. Chem. Abs.* **A**, 1935, 605.

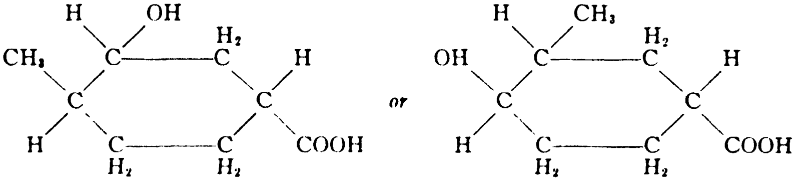
[44] British P. 352,164, 1931 and 438,810, 1935, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, **B**, 1931, 962; 1936, 137; *Chem. Abs.*, 1932, **26**, 3261; 1936, **30**, 3220; *J. Inst. Pet. Tech.*, 1936, **22**, 55A.

[45] E. Lehmann and W. Paasche, *Ber.*, 1935, **68**, 1068; *Brit. Chem. Abs.* **A**, 1935, 974; *Chem. Abs.*, 1935, **29**, 5428.



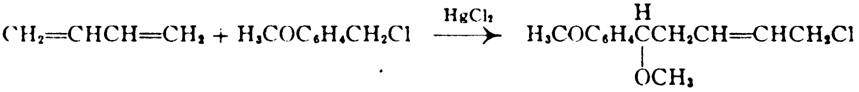
(*m.p., 135-140°C.*)

This 1,4 addition is also accompanied by the formation of a small amount of 3(4)-methyl-4(3)-hydroxy-cyclohexane-1-carboxylic acid:



(*m.p., 156°C.*)

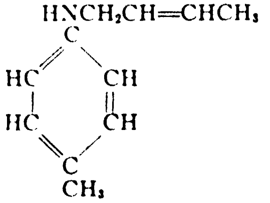
Other types of condensations of conjugated diolefins have been studied by Straus and Thiel.[46] They prepared 1-anisyl-1-methoxy-5-chloro-3-pentene (b.p., 104°C. at 0.1 mm.) by treating butadiene (in the presence of mercuric chloride) with *p*-methoxy-benzylchloride.



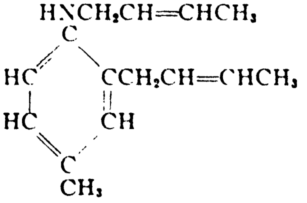
$$CH_2{=}CHCH{=}CH_2 + H_3COC_6H_4CH_2Cl \xrightarrow{HgCl_2} H_3COC_6H_4\overset{H}{C}(OCH_3)CH_2CH{=}CHCH_2Cl$$

In addition, these workers also obtained such compounds as 1-phenyl-1-methoxy-5-chloro-3-pentene (b.p., 126-127°C. at 12 mm.) and 1-methoxy-5-chloro-3-pentene (b.p., 56°C. at 10 mm.).

Interactions of butadiene with aryl amines were reported by Hickinbottom,[47] who heated aniline solutions of butadiene (8 to 12 per cent) in the presence of aniline hydrochloride or hydrobromide in a sealed tube at 220 to 260°C. for 4 to 25 hours. From the resulting mixture, 1-*p*-aminophenyl butene-2 (b.p., 135-136°C. at 24 mm.), 1-phenylamino butene-2 (b.p., 132-134°C. at 34 mm.) and 2,3-dimethyl-indole (m.p., 105-106°C.) were separated. In a similar manner, *p*-toluidine and butadiene furnished 2,3,5-trimethylindole (m.p., 120-121°C.) and the following compounds:



(*b.p., 135°C. at 33 mm.*)



(*b.p., 185°C. at 30 mm.*)

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[46] F. Straus and W. Thiel, *Ann.*, 1936, **525**, 151; *Brit. Chem. Abs.* **A**, 1936, 1375; *Chem. Abs.*, 1937, **31**, 363.

[47] W. J. Hickinbottom, *J.C.S.*, **1934**, 1981; *Chem. Abs.*, 1935, **29**, 1399; *Brit. Chem. Abs.* **A**, 1935, 205.

The autopolymerization of butadiene has been observed by Khokhlovkin[48] to be complete in 515 days, if light is present. It was found that 427 days were required to produce enough polymer to catalyze the reaction to a more appreciable rate than during this period. That is, it was noted that about 85 per cent of the polymers were formed in the final relatively short period of 88 days.

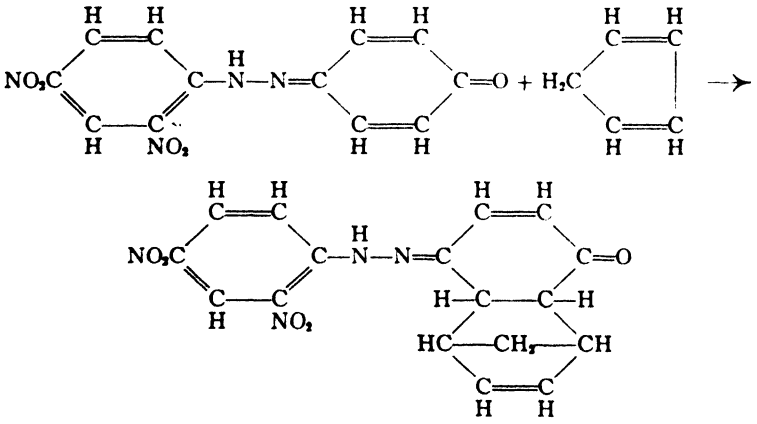
Days	Per Cent of Polymer Formed
427	14.8
486	62.5
515	100.0

The speed of autopolymerization in the absence of light was found to decrease considerably.

CYCLODIENE CONDENSATION REACTIONS

Cyclopentadiene[49] has been found to add to certain hydroxyazo compounds. Lauer and Miller[50] provided definite evidence that the latter show a quinoid character by means of such condensations.[51]

Addition of 2,4-dinitro-benzeneazophenol to cyclopentadiene was carried out in various concentrations of sodium acetate and chloroacetic acid in glacial acetic acid. After being refluxed on steam baths for about 3 hours (5 hours in one case) these mixtures were then cooled at 10-15°C. for 10 days in order to crystallize the crude product. Purification was effected by recrystallization from either acetic acid, ethyl acetate, pyridine or acetic anhydride. The reaction may be represented as:



In Table 150, the results of carrying out this reaction in the various media are shown. The yields of addition product show an increase with increased chloroacetic acid content of the glacial acetic acid.

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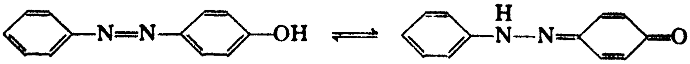
[48] M. A. Khokhlovkin, *Sintet. Kauchuk*, 1936 (4), 12; *Chem. Abs.*, 1936, 30, 6602.

[49] See Chapter 26 for a discussion of the structure and kinetics of formation of the cyclopentadiene polymers.

[50] W. M. Lauer and S. E. Miller, *J.A.C.S.*, 1935, 57, 520; *Brit. Chem. Abs.* A, 1935, 613; *Chem. Abs.*, 1935, 29, 2931.

[51] It will be remembered that the hydroxyazo compounds have been observed to show the tautomeric quinoid form



which reacts with 1,3-conjugated dienes.

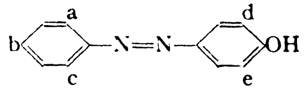
TABLE 150.—*Addition of Cyclopentadiene (3 cc.) to 2,4-Dinitrobenzeneazophenol (1.440 grams).*

Solvent (20 cc.)[a]	Yield of Addition Compound Grams	 %
1*M* CH_3COONa	0.358	20.2
	.355	20.1
CH_3COOH	0.490	27.7
	.540	30.5
	.550	31.1
	.503	28.4
1*M* $ClCH_2COOH$	0.653	36.9
	.656	37.1
	.667	37.7
2*M* $ClCH_2COOH$	0.836	47.2
	.860	48.6
	.803	45.4
	.781	44.1

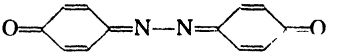
[a] This was glacial acetic acid to which was added sodium acetate, mono- or dichloroacetic acid.

However, Lauer and Miller state that not all *p*-hydroxyazo compounds combine with cyclopentadiene. He lists a number of these which are shown in Table 151. The letters *a, b, c,* etc., represent points at which substitution occurred while under each letter is placed the substituting group. For example, compound (1) was a dinitrodibromohydroxyazo benzene. Other compounds condensing with cyclopentadiene investigated by these experimenters include 2',4'-dinitro-4-hydroxy-2-bromoazobenzene and quinoneazine,

TABLE 151.—*Hydroxyazo Compounds Forming No Addition Products with Cyclopentadiene.*



	a	b	c	d	e
(1)	NO_2	NO_2		Br	Br
(2)	NO_2				
(3)	NO_2	Br			
(4)		NO_2			
(5)	NO_2	COOH			
(6)	Br	NO_2	Br		
(7)	COOH				
(8)		SO_3H			
(9)				COOH	
(10)		OH			



Cyclohexadiene condensation reactions have been studied by Straus and Thiel.[52] These workers reported additions (in the presence of mercuric chloride) with α-methoxy-benzylchloride to form ω-methoxy-benzyl-chloro-cyclohexene (b.p., 112°C. at 0.1 mm.), and monochlorodimethyl ether to form ω-methoxy-methyl-chlorocyclohexene (b.p., 81°C. at 10 mm.) These two compounds were believed to be a mixture of 1,2 and 1,4 addition products as shown by the following formulas, in which R may be either a phenyl group or a hydrogen atom.

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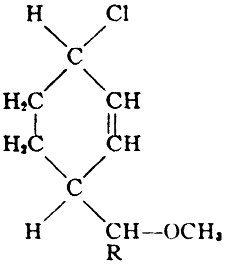
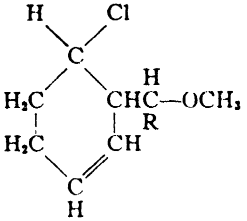
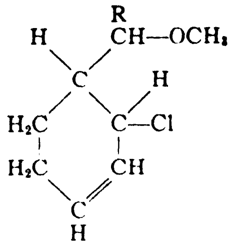
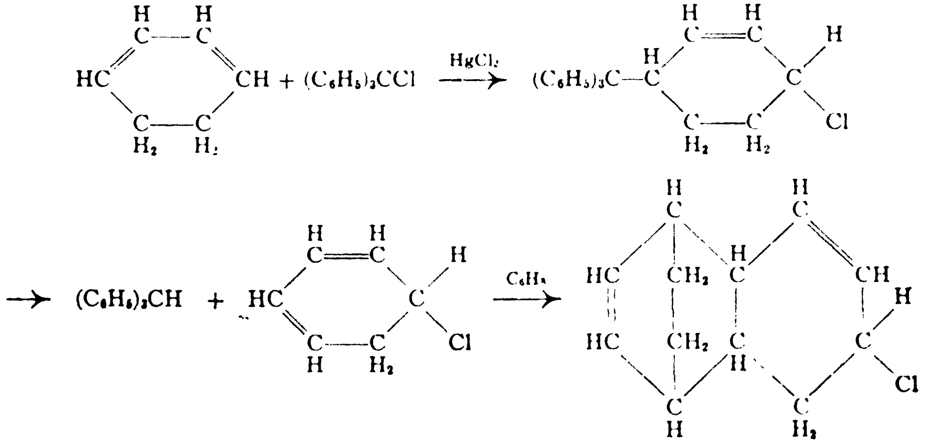
[52] F. Straus and W. Thiel, *Ann.*, 1936, 525, 151; *Brit. Chem. Abs.* A, 1936, 1375; *Chem. Abs.*, 1937, 31, 363.







The anisyl derivative of the last named compound was also prepared. An interesting reaction took place between cyclohexadiene and triphenyl-chloro-methane. The first step seemed to be a direct addition followed by the splitting off of triphenyl methane, which was isolated. The chloro-derivative formed appeared to unite with another molecule of cyclopentadiene to produce a monochloro-1,4-endoethylene-1,4,5,6,9,10-hexahydronaphthalene. One of the possible courses of this series of reactions is illustrated below:



Butadiene Sulphones

Sulphur dioxide readily combines with butadiene homologues to form sulphones.[53] In the experiments of Backer and Strating,[54] the reaction between 2,3-dimethyl-1,3-butadiene and an ethyl ether solution of sulphur dioxide at 100°C. resulted in a 60 per cent yield of the sulphone, 3,4-dimethyl-1-thia-3-cyclopentene 1,1-dioxide (m.p., 135°C.). In the same manner 1,2,3,4-tetramethyl-1,3-butadiene gave 2,3,4,5-tetramethyl-1-thia-3-cyclopentene 1,1-dioxide (m.p., 58-59°C.). Bromination of the first compound in carbon tetrachloride followed by treatment with hot normal sodium hydroxide solution yielded the corresponding *trans*-diol derivative. On the other hand, the *cis*-diol was formed by omitting the bromination step. These workers also prepared the sulphones of other butadiene homologues. For example, 2-phenylbutadiene combined with sulphur dioxide in ethyl ether yielded 3-phenyl-1-thia-3-cyclopentene 1,1-dioxide. In equation form,

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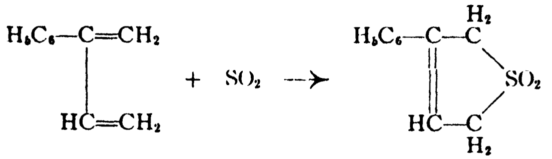
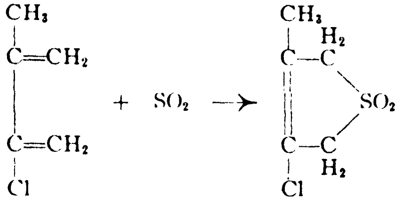
[53] For previous work see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co. Inc., New York, 1934, 654.

[54] H. J. Backer and J. Strating, *Rec. trav. chim.*, 1934, 53, 525; 1935, 54, 170; *Brit. Chem. Abs.* A, 1934, 662; 1935, 497; *Chem. Abs.*, 1934, 28, 4697; 1935, 29, 2959.



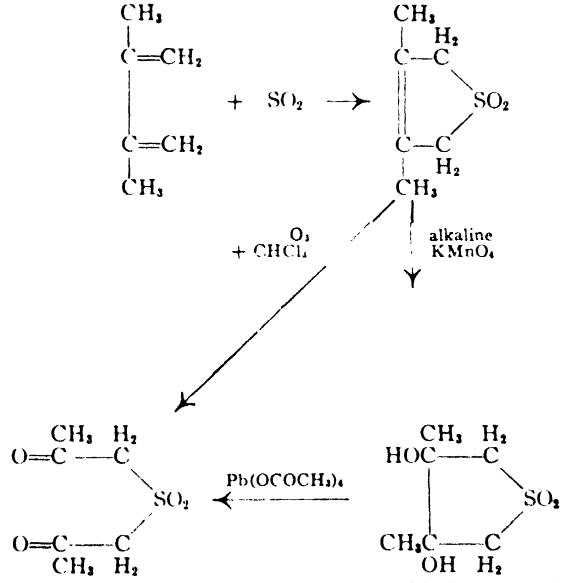
(*b.p., 58-59°C. at 9 mm.*) (*m.p., 132.5-133.5°C.*)

Also 2-chloro-3-methyl-butadiene similarly treated resulted in 4-chloro-3-methyl-1-thia-3-cyclopentene 1,1-dioxide. This is represented as follows:



(*m.p., 120-120.5°C.*)

Zuydewijn and Böeseken[55] obtained 2,3-dimethyl-3-thia-cyclopentene 1,1-dioxide from 2,3-dimethyl-1,3-butadiene and sulphur dioxide. Oxidation of the product by alkaline potassium permanganate yielded the *trans*-diol, which, in the presence of lead tetraacetate, was further oxidized to diacetonyl sulphone. The structure of the latter compound was confirmed by oxidation of the sulphone, in chloroform solution, with ozone. The various steps are indicated in the following manner:



diacetonyl sulphone (*m.p., 43°C.*)

trans-3,4-dihydroxy-3,4-dimethyl-1-thiacyclopentane 1,1-dioxide (56)

According to Böeseken and Zuydewijn,[57] butadiene sulphone, in 0.5*N* potassium hydroxide, exists in two isomeric forms. Either of these are hydrated, in alkaline solution to give a hygroscopic hydroxysulphone.

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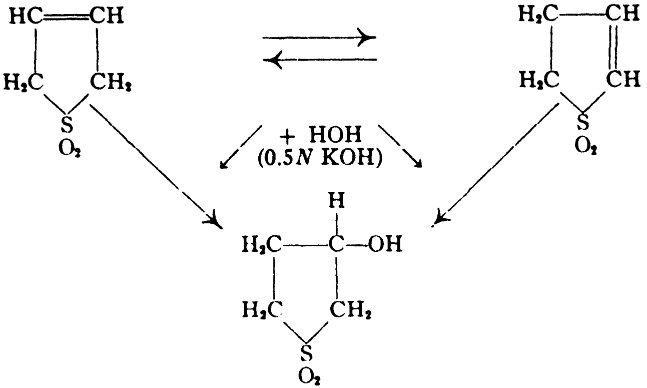
[55] E. van Zuydewijn and J. Boeseken, *Rec. trav. chim.*, 1934, **53**, 673; *Chem. Abs.*, 1934, **28**, 4697; *Brit. Chem. Abs.* **A**, 1934, 900.

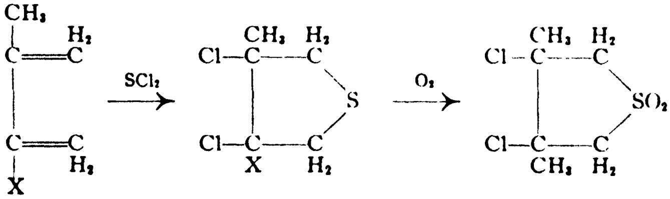
[56] For nomenclature of organic compounds see A. M. Patterson, *J.A.C.S.*, 1933, **55**, 3905; *Chem. Abs.*, 1933, **27**, 5304.



(m.p., 35°C.)

Furthermore, this alcohol is not converted (in potassium hydroxide solution) into either form of butadiene sulphone by the action of ultraviolet light. These experimenters therefore concluded that the tautomeric conversion of the above sulphone does not take place by the addition and separation of water, as was suggested by Backer and Strating.[58]

Sulphones may be prepared also by the interaction of conjugated diolefins with sulphur chloride followed by oxidation of the resulting product. Thus, Backer and Strating[59] reacted sulphur chloride with 2,3-dimethylbutadiene in an ice-salt bath for several hours and procured 3,4-dichloro-3,4-dimethyl-thiacyclopentane. This compound, when dissolved in acetic acid and treated with oxygen, was converted into the sulphone, 3,4-dichloro-3,4-dimethyl-1-thiacyclopentene 1,1-dioxide [m.p., 265°C. (decomposes)]. In a similar manner, isoprene furnished 3,4-dichloro-3-methyl-thiacyclopentene 1,1-dioxide (m.p., 144.5-145.5° C.). These reactions may be represented as follows, where X represents either hydrogen or a methyl group.



Miscellaneous Reactions of Diolefins

Allene reacts with nitrogen trioxide in cold ether, according to Dem'yanov and Ivanov,[60] to form a crystalline nitrosite, $C_3H_4N_2O_3$ (m.p., 89°C., decomposition),

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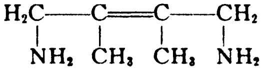
[57] J. Böeseken and E. van Zuydewijn, *Proc. Acad. Sci. Amsterdam*, 1936, **39**, 31; *Chem. Abs.*, 1936, **30**, 3403; *Brit. Chem. Abs.* **A**, 1936, 589.

[58] H. J. Backer and J. Strating, *Rec. trav. chim.*, 1935, **54**, 618; *Chem. Abs.*, 1936, **30**, 3403; *Brit. Chem. Abs.* **A**, 1935, 1105.

[59] H. J. Backer and J. Strating, *Rec. trav. chim.*, 1935, **54**, 52; *Brit. Chem. Abs.* **A**, 1935, 325; *Chem. Abs.*, 1935, **29**, 2504.

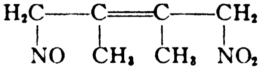
[60] N. Y. Dem'yanov and A. A. Ivanov, *Compt. rend. acad. sci. U.R.S.S.*, 1934, **1**, 318; *Chem. Abs.*, 1934, **28**, 4374; *Brit. Chem. Abs.* **A**, 1934, 508. See also Carleton Ellis, *loc. cit.*, 580, for reactions of nitrogen trioxide with olefins.

and a very unstable liquid. Purification of the nitrosite was effected by recrystallizing from hot acetic acid. These investigators also isolated the nitrosite $C_6H_{10}N_2O_3$ (m.p., 104-105°C.) and a liquid product from the reaction between nitrogen trioxide and dimethylbutadiene. The liquid was converted to a diamine (by tin and hydrochloric acid) which affected polarized light. The hydrogen chloride salt when heated in a test tube gave evidence of the pyrrole reaction. With these reactions as a basis, the structure of the amine was suggested as



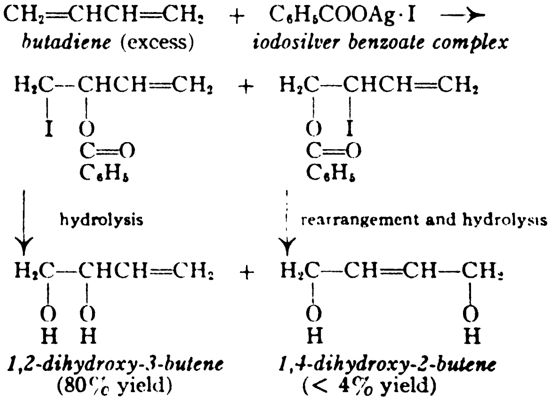
$$\begin{array}{cccc} H_2C & -\!\!-C & =\!\!=C & -\!\!-CH_2 \\ | & | & | & | \\ NH_2 & CH_3 & CH_3 & NH_2 \end{array}$$

and for the original liquid

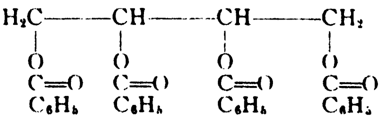


$$\begin{array}{cccc} H_2C & -\!\!-C & =\!\!=C & -\!\!-CH_2 \\ | & | & | & | \\ NO & CH_3 & CH_3 & NO_2 \end{array}$$

Although the example of a 1,4-addition just given is of the general reaction type, there are exceptions. For example, the action of iodosilver benzoate[61] on an excess of butadiene was found to result in mainly the 1,2 union. The determination was made by hydrolyzing the resulting mixture and separating out 1,2-dihydroxy-3-butene in an 80 per cent yield and 1,4-dihydroxy-2-butene in less than 4 per cent yield. Therefore it was concluded by Prévost and Lutz[62] that the complex added mainly to the 1 and 2 positions rather than the 1 and 4. That the latter addition product was not obtained as a major intermediate in the experiments was explained by suggesting that the iodine would probably migrate to the 4 position, as bromine does. The reactions are represented below:


$CH_2{=}CHCH{=}CH_2$ + $C_6H_5COOAg{\cdot}I$
butadiene (excess)
iodosilver benzoate complex
hydrolysis
rearrangement and hydrolysis
1,2-dihydroxy-3-butene
(80% yield)
1,4-dihydroxy-2-butene
(< 4% yield)

Using an excess of the silver complex, a 60 per cent yield of mesotetrabenzoylerythritol (m.p., 187°C.) was secured. This may be represented by the following:



$$\begin{array}{cccc} H_2C & -\!\!-CH & -\!\!-CH & -\!\!-CH_2 \\ | & | & | & | \\ O & O & O & O \\ C{=}O & C{=}O & C{=}O & C{=}O \\ C_6H_5 & C_6H_5 & C_6H_5 & C_6H_5 \end{array}$$

meso-tetrabenzoylerythritol

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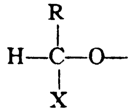
[61] According to H. Wieland. F. G. Fischer (*Ann.*, 1925, 446, 49; *Chem. Abs.*, 1926, 20, 408), silver benzoate, $(C_6H_5)COOAg$, in ether or benzene suspension, absorbs 1 equivalent of iodine at room temperature to form iodosilver benzoate. This complex decomposes in water to give benzoic acid, silver iodide and silver iodate.

[62] C. Prévost and R. Lutz, *Compt. rend.*, 1934, 198, 2264; *Chem. Abs.*, 1934, 28, 6105; *Brit. Chem. Abs.* A, 1934, 989.

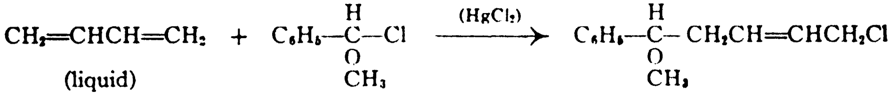
According to Carpenter,[63] dicarboxylic acids can be produced by the combination of diolefins and formic acid. Limits of conditions recommended are pressures of 25 to 900 atmospheres and temperatures of 100-500°C.

Halogenated ethers have been obtained by the combination of butadiene and alkoxyalkyl halides of the general formula



$$H-\overset{\displaystyle R}{\underset{\displaystyle X}{C}}-O-R^1$$

where R is hydrogen, alkyl, aryl or aralkyl group, R^1 is alkyl, aryl or aralkyl group, and X is a halogen atom.[64] An example of this type of reaction is that of butadiene with methoxybenzyl chloride, employing mercuric chloride as a catalyst.



$$\underset{\text{(liquid)}}{CH_2{=}CHCH{=}CH_2} + C_6H_5-\overset{\displaystyle H}{\underset{\displaystyle \overset{O}{CH_3}}{C}}-Cl \xrightarrow{(HgCl_2)} C_6H_5-\overset{\displaystyle H}{\underset{\displaystyle \overset{O}{CH_3}}{C}}-CH_2CH{=}CHCH_2Cl$$

1-phenyl-1-methoxy-5-chloro-3-pentene
(b.p., 93°C./0.01 mm.)

Among the other compounds[65] that were produced in a similar manner are 1-methoxy-5-chloro-3-pentene (b.p., 118°C.), 1-phenyl-1-methoxy-5-bromo-3-pentene (b.p., 92°C. at 0.05 mm.) and 1-methoxybenzyl-2-chlorocyclohexane (b.p., 94.5°C. at 0.01 mm.)

Passage of the diolefin into an ether solution of thiocyanogen is said to result in an 80 per cent yield of the dithiocyano derivative.[65a] Addition in this instance takes place normally, i.e., in the 1,4-positions, and is so rapid that polymerization (of butadiene) is largely avoided.

$$CH_2{=}CHCH{=}CH_2 + (SCN)_2 \longrightarrow CH_2(SCN)CH{=}CHCH_2(SCN)$$

Interaction of this product with halogens (chlorine or bromine) in acetic acid as a solvent gives rise to 2,3-dihalogenated compounds. With chlorine this may be represented by

$$CH_2(SCN)CH{=}CHCH_2(SCN) + Cl_2 \longrightarrow CH_2(SCN)CHClCHClCH_2(SCN)$$

1,4-Dithiocyanobutene, however, undergoes decomposition when boiled with solutions of caustic soda, one of the substances formed being sodium sulphide.

Reduction of diolefins to monolefins may be effected by treating the former successively with an alkali metal and an amine.[65b] Thus, butadiene may be dissolved in ether at −10° to 20°C., and reacted with lithium and ethylaniline. Under these conditions the product is said to consist mainly of *cis*-1,2-dimethylethylene.

ANALYTICAL REACTIONS OF CONJUGATED DIENES

The use of maleic anhydride as a reagent in the determination of conjugated diolefins in complex gas mixtures has been the object of considerable experimentation.[66] However, its application in a quantitative analysis has been limited. Korotkov[67] has described an apparatus for the determination of butadiene in a gas mixture. The latter, during the course of analysis, passes through a U-shaped tube containing maleic anhydride which is kept in a molten state by immersing the tube in boiling water. The diolefin is absorbed by the condensation with the reagent.

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[63] G. B. Carpenter, Canadian P. 339,932, 1934; *Chem. Abs.*, 1934, **28**, 3082.

[64] British P. 446,222, 1936, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1936, 824; *Chem. Abs.*, 1936, **30**, 6760; French P. 788,341, 1935; *Chem. Abs.*, 1936, **30**, 1387.

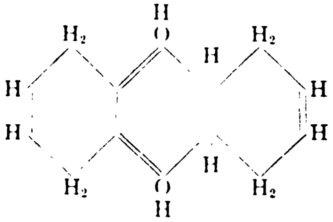
[65] The preparation of butadiene alkoxy derivatives from vinylacetylene has been described by I. A. Rotenberg and M. A. Favorskaya (*J. Gen. Chem.* (*U.S.S.R.*), 1936, **6**, 185; *Chem. Abs.*, 1936, **30**, 4808; *Brit. Chem. Abs.* **A**, 1936, 964).

[65a] E. Müller and A. Freytag, *J. prakt. Chem.*, 1936, **146**, 58; *Chem. Abs.*, 1936, **30**, 7537; *Brit. Chem. Abs.* **A**, 1936, 1228.

[65b] K. Ziegler, F. Häffner and H. Grimm, *Ann.*, 1937, **528**, 101; *Brit. Chem. Abs.* **A** (2), 1937, 173.

Because of its reactivity with other conjugated diolefins, maleic anhydride can be applied only when one particular diolefin is present. For example, Tropsch and Mattox[68] have offered a procedure for quantitatively determining butadiene in gases when no other diolefins are present. These workers found that the presence of monolefins or acetylene in concentrations up to 15 per cent did not influence the accuracy of the analysis. Dolgoplosk[69] has used a rapid hydrogenation method in the analysis of butadiene in gaseous products intended for use in the manufacture of synthetic rubber. In this investigation he passed the gas diluted with hydrogen over a catalyst, either nickel (50 per cent) or palladium (30 per cent) precipitated on asbestos, and observed the change in volume. It was noted that the presence of 0.03 per cent of carbon monoxide caused the catalyst to become poisoned unless the latter was heated.

Butadiene has been determined by condensation with quinones in the presence of other olefins, ether and acetic acid.[70] The gas to be analyzed was conducted through a phenol solution of benzoquinone to furnish a thick black oil, believed to be 1,4,5,8-tetrahydroanthrahydroquinone:



Sorokin and Puzitzkii[71] have shown that the action of liquid sulphur dioxide on butadiene cannot be adapted to the quantitative determination of the latter compound.

The estimation of olefins and diolefins with halogens and halogen acids has been previously proposed.[72] Sorokin, Belikova and Bogdanova[73] report that the method of Ipatieff and Vittorf[74] for the determination of isoprene can be applied to butadiene. The procedure is based on the formation of the monobromide (b.p., 103°C.) and dibromide (b.p., 170-172°C.) of butadiene from the action of hydrobromic acid in glacial acetic acid.[75]

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[66] For a discussion of early work see, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**, 659; "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**, 830.

[67] A. A. Korotkov, *Sintet. Kauchuk*, **1933** (4), 23; *Chem. Abs.*, 1934, **28**, 3028.

[68] H. Tropsch and W. J. Mattox, *Ind. Eng. Chem.*, *Anal. Ed.*, 1934, **6**, 104; *Chem. Abs.*, 1934, **28**, 3029; *Brit. Chem. Abs.* **B**, 1934, 390. See Chapter 49 for a description of this method.

[69] B. A. Dolgoplosk, *Sintet. Kauchuk*, **1935** (5), 11; *Chem. Abs.*, 1936, **30**, 410.

[70] B. A. Dolgoplosk, *Sintet. Kauchuk*, **1934** (2), 29; *Chem. Abs.*, 1935, **29**, 3941. See also Chapter 49 for other determinations of butadiene.

[71] V. A. Sorokin and K. V. Puzitzkii, *Sintet. Kauchuk*, **1933** (6), 12; *Chem. Abs.*, 1934, **28**, 3339.

[72] Carleton Ellis, *loc. cit.*

[73] V. Sorokin, A. Belikova and O. Bogdanova, *J. Rubber Ind.* (*U.S.S.R.*), 1931, **5**, (4-5), 26; *Chem. Abs.*, 1933, **27**, 5680; *Brit. Chem. Abs.* **A**, 1934, 313; *Chem. Zentr.*, 1932, 1, 1932.

[74] V. N. Ipatieff and N. von Vittorf, *J. Russ. Phys. Chem. Soc.*, 1897, **29**, 132; *J.C.S.*, 1897, **72**, 233; *J.S.C.I.*, 1897, **16**, 248; *J. prakt. Chem.*, 1897, **55**, 1.

[75] The compounds which have nearly the same composition and have similar boiling ranges are bromocyclobutane (b.p., 102-104°C.) and 1,3-dibromobutane (b.p., 173-174°C.) as reported by W. H. Perkin, Jr. (*J.C.S.*, 1894, **65**, 950; *Chem. Zentr.*, 1895, **1**, 25).

In his study of cyclopentadiene and dicyclopentadiene, Schultze[76] found that these two compounds absorb oxygen within a very short time to such an extent that any quantitative bromination of these hydrocarbons is rendered inaccurate.[77] He stated that the addition of bromine is dependent upon the peroxide content of the material. That is, "no quantitative results are found whenever the experimental conditions are such as to permit peroxide formation previous to bromination." With this in mind, he presented three methods of analysis of cyclopentadiene and dicyclopentadiene. The first of these was a modified bromide-bromate titration using 0.4 *N* sulphuric acid in a vacuum titration bottle. The second was a bromine-water titration also in a vacuum bottle. In the third method, the titration was carried out in the presence of air with an excess of free bromine present in solution before the capsule containing the material to be analyzed was broken.

Cyclopentadiene can be determined in mixtures with its polymers by means of its reaction with *p*-nitrobenzenediazonium chloride in acetic acid solution.[78]

Diazotized *p*-nitroaniline has also been found to react quantatively with conjugated dienes but only when these are admixed with saturated hydrocarbons.[79] The excess diazo reagent is back-titrated with β-$C_{10}H_7OH$. 2,3-Dimethyl-1,3-butadiene, 1,3-cyclohexadiene and cyclopentadiene are among those diolefins which may be estimated in this manner.

A report of a color reaction for the detection of very small quantities of cyclopentadiene has been announced by Afanas'ev.[80] His procedure involves the use of one drop of the specimen mixed with 1 cc. each of chloroform and glacial acetic acid and then treated cautiously with 2 or 3 drops of concentrated sulphuric acid. As little as 0.1 milligram of cyclopentadiene gives a distinct violet coloration.

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[76] G. R. Schultze, *J.A.C.S.*, 1934, **56**, 1552; *Brit. Chem. Abs.* **A**, 1934, 995; *Chem. Abs.*, 1934, **28**, 5047.

[77] H. Staudinger and A. Rheiner (*Helv. Chim. Acta*, 1924, 7, 23; *Chem. Abs.*, 1924, **18**, 1275; *J.C.S.*, 1924, **126** (1), 274) obtained results from the bromination of these substances which indicated that there was incomplete saturation of the double bonds.

[78] A. P. Terent'ev and L. A. Solokhin, *Sintet. Kauchuk*, **1933** (5), 12; *Chem. Abs.*, 1934, **28**, 3338.

[79] A. P. Terent'ev, E. V. Vinogradova and G. D. Hal'pern, *Compt. rend. acad. sci. U.R.S.S.*, 1935 **4**, 267; *Brit. Chem. Abs.* **A**, 1936, 744; *Chem. Abs.*, 1936, **30**, 3746.

[80] B. N. Afanas'ev, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 15; *Chem. Abs.*, 1936, **30**, 1330; *Brit. Chem. Abs.* **A**, 1936, 321; *J. Inst. Pet. Tech.*, 1936, **22**, 91A.

Chapter 28

Important Reactions of Acetylene

Acetylene, HC≡CH, is the simplest member of the alkyne series of hydrocarbons possessing the general formula C_nH_{2n-2}. Its homologues may be placed roughly into two classes in which one, or both, of the hydrogen atoms of acetylene are replaced by alkyl or aryl groups. Because of its unsaturated and unstable character, acetylene lends itself to a great variety of reactions, making it the starting point for the synthesis of a number of important products.[1]

Although the major proportion of commercial acetylene is obtained by the hydrolysis of calcium carbide, significant quantities can be produced by the electrical and thermal decomposition of gaseous hydrocarbons from petroleum as described in Chapters 4 and 9.[2] To the layman the familiar application of acetylene is as a gas for illuminating purposes and for welding by means of the oxy-acetylene flame,[3] but to the chemist a more interesting use is as raw material for the preparation of a wide variety of organic compounds.[4] Among these are acetaldehyde, acetic acid, acetone, vinyl esters and ethers, acetals and various halogenated hydrocarbons as well as synthetic drying oils, synthetic rubber and synthetic resins.[5] By-products in the acetaldehyde, acetic acid and acetone syntheses include biacetyl, acetonylacetone, 2,5-dimethylfuran, acetylmethylcarbinol, 1,3-butene glycol, ethyl β-hydroxybutyrate and 4-methyl- and 5-methyl-2,3-dihydroxybenzaldehyde.[6] (See Fig. 153)

Acetylene is a colorless gas, possessing a pleasant ethereal odor.[7] Because of its endothermic nature acetylene cannot be stored in cylinders under high pressure but it may be kept under 10 atmospheres pressure by dissolving it in acetone absorbed on a porous mass.[8] The high solubility of the hydrocarbon in acetone, 24 volumes at 15°C. under 1 atmosphere, is of course well known.[9] Proposals for the use of acetone solutions of acetylene with alcohol and with furfural as motor fuels have been made.[10]

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[1] A review of developments of acetylene chemistry is given by O. Nicodemus, *Angew, Chem.*, 1936, **49**, 787; *Chem. Abs.*, 1937, **31**, 477.

[2] It is interesting to note that an azeotropic mixture of acetylene (40.7 per cent) and ethane (59.3 per cent) has been isolated from reformed refinery gases (W. A. McMillan, *J.A.C.S.*, 1936, **58**, 1345; *Chem. Abs.*, 1936, **30**, 6702).

[3] A comparison of oxyacetylene flames with other fuel gases for cutting purposes has been described by G. V. Slottman (*36th Ann. Convention, Intern. Acetylene Assoc. (Cleveland)*, 1935; *Chem. Abs.*, 1936, **30**, 2149).

[4] For a brief discussion see J. A. Nieuwland, *Ind. Eng. Chem.*, 1935, **27**, 851.

[5] For a discussion of the latter three types of products see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[6] A. F. G. Cadenhead, *Can. Chem. Met.*, 1935, **19** (12), 325; *Chem. Abs.*, 1936, **30**, 1143. G. Benson and A. F. G. Cadenhead, *J.S.C.I.*, 1934, **53**, 40T.

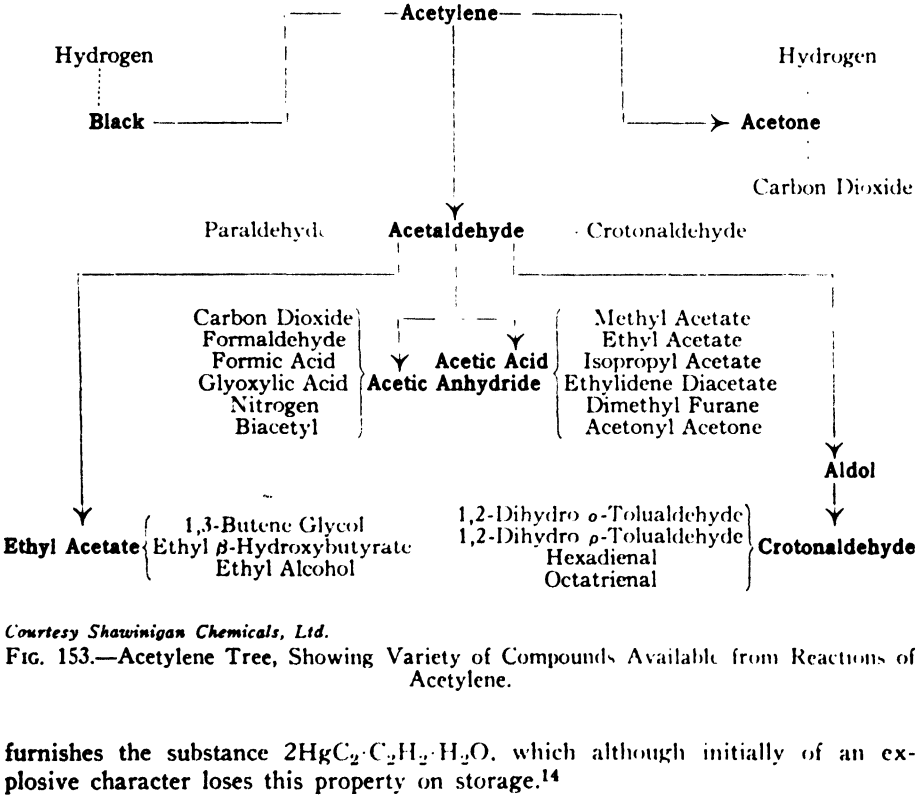
[7] For an extensive description of the physical and chemical properties of acetylene, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934. A method for the determination of small amounts of acetylene in butadiene or nitrogen has been developed by T. F. Chernyakovskaya (*Sintet. Kauchuk*, 1936 (2), 29; *Chem. Abs.*, 1936, **30**, 6309).

[8] See, in this instance, H. P. Rauert, *Azetylene Wiss. Ind.*, 1932, **35**, 97; *Chem. Abs.*, 1934, **28**, 5209. The explosive nature of acetylene has been discussed by W. C. de Liefde (*Chem. Weekblad*, 1934, **31**, 711; *Brit. Chem. Abs.* B, 1935, 835; *Chem. Abs.*, 1935, **29**, 3161) and A. Krauss (*Autogene Metallbearbeit*, 1935, **28**, 72; *Brit. Chem. Abs.* B, 1936, 818; *Chem. Zentr.*, 1935, **2**, 563).

[9] For a discussion of the solubility of acetylene at 50 to 760 mm. pressures in dichloroethane, 97 per cent ethyl alcohol and heavy naphtha (b.p., 150-250°C.) at 0°C. and in kerosene at 0°C. or 20°C., see V. A. Kireev and M. A. Romanchuk (*J. Gen. Chem.* (*U.S.S.R.*), 1936, **6**, 78; *Chem. Abs.*, 1936, **30**, 7421).

[10] J. Arauz, *Anales univ. central Ecuador*, 1933, **50**, 179; *Chem. Abs.*, 1934, **28**, 5955. J. M. H. Classen, German P. 615,651, 1935; *Chem. Abs.*, 1935, **29**, 8294. See also Chapter 44.

Much interest has been shown in the products formed by the reaction of acetylene with salts of mercury, particularly since the latter have been employed as catalysts in the hydration of acetylene to acetaldehyde or its condensation with hydroxy compounds and with organic acids. The composition of the complex salt resulting from the interaction of acetylene and mercuric chloride has caused some controversy. For instance several workers stated that the compound $C_2(HgCl)_2$ was formed.[11] Others reported obtaining a substance $C_2Hg_3Cl_4$ which hydrolyzed rapidly to $C(HgCl)_3CHO$, trichloromercuriacetaldehyde.[12] Later work[13] has indicated the composition of the product to be $HgC_2 \cdot HgCl_2 \cdot HgCl$. When treated with a saturated solution of mercuric acetate in acetic acid, acetylene furnishes the substance $2HgC_2 \cdot C_2H_2 \cdot H_2O$, which although initially of an explosive character loses this property on storage.[14]



Courtesy Shawinigan Chemicals, Ltd.

FIG. 153.—Acetylene Tree, Showing Variety of Compounds Available from Reactions of Acetylene.

POLYMERIZATION OF ACETYLENE

Polymerization and decomposition of acetylene present a field of chemical investigation in which a wide variety of conditions may be employed. Means of inducing reaction include chemical reagents, heat, electrical discharges, alpha particles, light rays, cathode rays and electromagnetic fields.[15] The products include gases, aliphatic and aromatic liquids, tars and solids. As will be pointed out later, controlled polymerization of acetylene yields unsaturated hydrocarbons (e.g., vinylacetylene) from which numerous diverse compounds can be synthesized.[16]

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[11] See E. H. Keiser, *Am. Chem. J.*, 1893, **15**, 535; *J.C.S.*, 1894, **66** (1), 61. The determination of acetylene in liquid air, using mercuric and potassium iodide, is described by L. M. Iol'son, I. I. Strizhevskii and A. B. Bergel'son, *Zavodskaya Lab.*, 1936, **5**, 952; *Chem. Abs.*, 1937, **31**, 337.

[12] K. A. Hofmann, *Ber.*, 1899, **32**, 870; 1904, **37**, 4459; *J.C.S.*, 1899, **76** (1), 485; 1905, **88** (1), 2. H. Biltz and O. Mumm, *Ber.*, 1904, **37**, 4417; *J.C.S.*, 1905, **88** (1), 2.

[13] E. Ferber and E. Römer, *J. prakt. Chem.*, 1934, (2) **139**, 277; *Brit. Chem. Abs.* **A**, 1934, 389; *Chem. Abs.*, 1934, **28**, 4332. W. Manchot and J. Haas, *Ann.*, 1913, **399**, 123; *Chem. Abs.*, 1913, **7**, 3483; *J.C.S.*, 1913, **104** (1), 1009.

[14] E. Ferber and E. Römer, *loc. cit.*

According to Toul[17] very pure acetylene does not polymerize when exposed to sunlight. Polymerization does take place, however, in ultraviolet light.[18] Although early investigators reported only solid polymers, later ones have noted the formation of benzene and other aromatic hydrocarbons as well as saturated and olefinic hydrocarbons in this treatment.[19] The empirical formula of the solid product obtained by the action of ultraviolet light on acetylene was calculated by Lind and Livingston[20] to be approximately $(C_{10}H_9)_n$. From this a mechanism of polymerization was suggested as follows:

$$\begin{aligned} C_2H_2 + h\nu &\longrightarrow C_2H_2 \longrightarrow C_2H + H \\ C_2H_2 + C_2H &\longrightarrow C_4H_3 \\ C_4H_3 + C_2H_2 &\longrightarrow C_6H_5, \text{ and so on.} \end{aligned}$$

The formation of benzene and related hydrocarbons was explained by side reactions:

$$\begin{aligned} C_8H_7 &\longrightarrow C_6H_6 + C_2H \\ \text{or } C_6H_5 + H &\longrightarrow C_6H_6 \end{aligned}$$

The polymerization of carefully purified acetylene at 750°C. was studied by Mignonac and Ditz.[21] The gas was passed rapidly through an electrically heated quartz tube and the products were immediately cooled to —70°C. giving a yellow liquid condensate consisting largely of benzene. Other constituents, obtained on fractional distillation of the condensate, included unreacted acetylene and two dimers, one a stable, colorless gas and the other a yellow unstable gas which was given the name "chlorene." It is said that a 90 per cent yield of benzene can be obtained if acetylene is preheated and then mixed with inert gases at 630°C. and the product cooled rapidly.[22] Under these conditions no tarring or carbonization occurs. Investigations of the polymerization of acetylene at 950-1050°C. have shown that the introduction of nitrogen has the same effect as would a reduction of pressure.[23] Hydrogen favors the formation of methane and the presence of the latter retards the development of more methane. This hydrocarbon, when present to the extent of 30 per cent or more, is a factor in the production of light and heavy oils from acetylene. Liquid diluents, for example decahydronaphthalene, may be employed.[24] In such cases reaction may be effected at pressures of 40-50 atmospheres and temperatures of 320-440°C.

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[15] Pyrolysis of acetylene is discussed in Chapters 2, 4 and 5. For use of electrical energy see Chapter 9.

[16] For reviews on the polymerization of acetylene see G. Egloff, C. D. Lowry, Jr. and R. E. Schaad. *J. Phys. Chem.*, 1932, **36**, 1457; *Chem. Abs.*, 1932, **26**, 1457; *Brit. Chem. Abs.* **A**, 1932, 717. and L. Neumann, *Ges. Abhandl. Kenntnis Kohle*, 1934, **11**, 404; *Chem. Zentr.*, 1934, **2**, 878. *Chem. Abs.*, 1935, **29**, 6568; *Brit. Chem. Abs.* **B**, 1935, 394. G. Egloff, "The Reactions of Pure Hydrocarbons," Reinhold Publishing Corp., New York, 1937.

[17] F. Toul, *Collection Czech. Chem. Communications*, 1934, **6**, 163; *Chem. Abs.*, 1934, **28**, 5745.

[18] For references to previous work see Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934, 667; "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935, 144.

[19] See, for example, R. Livingston and C. H. Schiflett, *J. Phys. Chem.*, 1934, **38**, 377; *Chem. Abs.*, 1934, **28**, 3663; *Brit. Chem. Abs.* **A**, 1934, 611. W. Kemula and S. Mrazek, *Z. physik Chem.*, 1933, **B23**, 358; *Brit. Chem. Abs.* **A**, 1934, 168; *Chem. Abs.*, 1934, **28**, 1603.

[20] S. C. Lind and R. Livingston, *J.A.C.S.*, 1934, **56**, 1550; *Brit. Chem. Abs.* **A**, 1934, 976; *Chem. Abs.*, 1934, **28**, 5337.

[21] G. Mignonac and E. Ditz, *Compt. rend.*, 1934, **199**, 367; *Chem. Abs.*, 1934, **28**, 6697.

[22] Y. Kato and H. Aikawa, *J. Elektrochem. Assoc. Japan*, 1935, **3**, 261; *Chem. Abs.*, 1936, **30**, 2555.

[23] H. Pichler, *Ges. Abhandl. Kenntnis Kohle*, 1934, **11**, 401; *Chem. Abs.*, 1935, **29**, 6568.

[24] M. Hofsäsz, U. S. P. 1,964,399, June 26, 1934, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 5082. German P. 592,858, 1934, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, **28**, 3421.

Simultaneous hydrogenation and polymerization of acetylene with mixed catalysts has been studied by Peters and Neumann.[25] By use of a mixture of 9 parts iron, 0.5 part nickel and 0.5 part copper and employing temperatures up to 190°C., a 64 per cent yield of liquid products resulted. Tungstic oxide, the rare earth oxides and iron oxide were not effective agents, although the latter was rendered active by the addition of nickel monoxide. According to Petrov and Antzus[26] employment of a reduced nickel catalyst yields a gasoline (end point 320°F.) containing about 40 per cent of naphthenic hydrocarbons.

When heated in the presence of copper, its oxides or alloys, acetylene yields a yellow-brown solid polymer of indefinite composition but of an aromatic nature. This material, known as cuprene or carbene, has been the subject of many investigations[27] both as to its nature and as to improvements in its manufacture. Depending upon the use for which it is intended, cuprene may be obtained as a soft, flocculent product or as a hard, brittle, porous mass. For example, acetylene mixed with 10-15 per cent nitrogen is passed over cuprous oxide containing one per cent stannic oxide. Soft products are obtained at 180-245°C. and a brittle material at 250-260°C.[28] Applications of cuprene include its utilization as an absorbent for fuels and illuminants and as a filler for linoleum and plastic masses.

Monovinylacetylene. Properly controlled low-temperature polymerization of acetylene will convert the hydrocarbon into monovinylacetylene, divinylacetylene and a tetramer, C_8H_8. One contact material which may be employed is an aqueous solution containing a mixture of a cuprous salt, an ammonium salt or a tertiary amine, and an inorganic acid.[29] The speed of contact between the hydrocarbon gas and catalyst may be varied so that monovinylacetylene is the main product. In a process developed by Chilton,[30] the resulting gases (containing acetylene and its polymers) are precooled to about 0°C. and dried by calcium carbide. Thus, further polymerization is said to be prevented. Separation from excess acetylene is effected by cooling to $-50°$ to $-80°$C. or by countercurrent extraction of monovinylacetylene with a mineral oil.[31] Modifications of the above-mentioned catalysts include the use of organic acids in place of inorganic[32] and the substitution of water by an inert non-aqueous solvent of high boiling point, e.g., glycerol or ethylene glycol.[33]

Perkins and Toussaint[34] converted acetylene into vinylacetylene by passing the gas at 70°C. into a nearly neutral aqueous solution of an alkali cuprochloride prepared from cuprous chloride and ammonium chloride or a chloride of an alkali metal or alkaline earth metal. With this type of mixture it has been also suggested[35] that the acidity be adjusted to a *p*H of about 6.0. In another method acid cuprous salt solutions free from nitrogen bases and containing salts of the alkali or alkaline-earth metals are employed.[36] The insoluble complex formed when acetylene is led into a solution containing 18 per cent cuprous chloride and 20 per cent ammonium chloride is said[37] to have the composition $6CuCl \cdot 3NH_4Cl \cdot C_2H_2$.

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[25] K. Peters and L. Neumann, *Ges. Abhandl. Kenntnis Kohle*, 1934, 11, 423; *Chem. Abs.*, 1935, **29**, 6567; *Brit. Chem. Abs.* B, 1935, 394; *Chem. Zentr.*, 1934, 2, 878. For energy and velocity constants in this type of reaction see H. A. Taylor and A. Van Hook, *J. Phys. Chem.*, 1935, **39**, 811; *Chem. Abs.*, 1935, **29**, 6205; *Brit. Chem. Abs.* A, 1935, 1082.

[26] A. D. Petrov and L. I. Antzus, *Refiner*, 1934, 13, 79; *Chem. Abs.*, 1934, **28**, 2170; *J. Inst. Pet. Tech.*, 1934, 20, 251A. *Compt. rend. acad. sci. U.R.S.S.*, 1934, 4, 295; *Chem. Abs.*, 1935, **29**, 2906; *Brit. Chem. Abs.* A, 1935, 325.

[27] For a detailed discussion see Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934. Also Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[28] R. H. Davis and L. A. Levy, British P. 418,005, 1934; *Brit. Chem. Abs.* B, 1935, 13.

[29] J. A. Nieuwland, U. S. P. 1,926,056, Sept. 12, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, **27**, 5750; *Brit. Chem. Abs.* B, 1934, 709. British P. 384,654, 1932 and addn. 390,179, 1932; *Chem. Abs.*, 1933, **27**, 4251, 4541; *Brit. Chem. Abs.* B, 1933, 182, 617. French P. 733,663, 1931, and addn. 41,454, 1931; *Chem. Abs.*, 1933, **27**, 2696.

[30] T. H. Chilton, U. S. P. 1,999,397, Apr. 30, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1936, 487; *Chem. Abs.*, 1935, **29**, 4022.

[31] British P. 401,678, 1933, addn. to 384,654, 1932 and 390,179, 1932, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1933, 182, 617; 1934, 136; *Chem. Abs.*, 1933, **27**, 4251, 4541; 1934, **28**, 2728; *J. Inst. Pet. Tech.*, 1934, **20**, 112A. French P. 43,351, 1934, addn. to 733,663, 1931; *Chem. Abs.*, 1934, **28**, 6727.

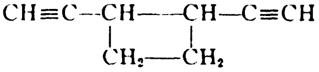
[32] J. A. Nieuwland and R. R. Vogt, U. S. P. 1,926,055, Sept. 12, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1934, 709.

[33] F. B. Downing, A. S. Carter and D. Hutton, U. S. P. 1,926,039, Sept. 12, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 5755.

[34] G. A. Perkins and W. J. Toussaint, U. S. P. 1,971,656, Aug. 28, 1934, to Carbide and Carbon Chem. Corp.; *Brit. Chem. Abs.* B, 1935, 714.

By passing acetylene at 300-800°C. over a catalyst, such as gold, molybdenum, silver or their alloys, or oxides of titanium, uranium or zirconium, monovinylacetylene and some aromatic compounds were formed.[38] Reaction may be effected by using a solid catalyst of a cuprous compound and a salt of an alkali or alkaline earth metal or ammonium salt.[39] With cuprous chloride and ammonium chloride precipitated on pumice, a 5 per cent yield of vinylacetylene (based on the acetylene used) was obtained at 200-250°C. At 350-400°C. the same yield was reported, using zinc chloride on pumice.[40]

According to Dykstra,[41] vinylacetylene can undergo at least three distinct types of polymerization. When heated without a catalyst at 105°C. for 6 hours, monovinylacetylene yields a mixed polymer in the form of a soft resin containing approximately 1 per cent dimer, 3 per cent trimer, 16 per cent tetramer, 8 per cent pentamer and 72 per cent higher polymers. The dimer in this case was thought to be diethinylcyclobutane:



$$\begin{array}{c} CH{\equiv}C{-}CH{-}{-}{-}CH{-}C{\equiv}CH \\ \quad\;\;\, | \qquad\quad | \\ \quad\;\;\, CH_2{-}{-}{-}CH_2 \end{array}$$

A similar thermal treatment of vinylacetylene with 1 to 10 per cent of acidic materials resulted in a 20-50 per cent yield of styrene. With cuprous chloride as catalyst, a dimer, 1,5,7-octatriene-3-yne, is formed.

With the aid of salts of mercury, silver, cadmium, copper or zinc in an acid solution (e.g., sulphuric, acetic, phosphoric), vinylacetylene can be hydrated to methyl vinyl ketone.[42] The reaction is assisted, according to Conaway,[43] by an oxidizing agent, e.g., ferric sulphate or oxide, copper sulphate, chromates, manganates and vanadates. A polymerization inhibitor, e.g., pyrogallol, eugenol or guaiacol, may be employed during distillation of the ketone. Using sodium alcoholates as catalysts, alcohols can be made to add smoothly to vinylacetylene at about 100°C. to give unsaturated ethers of the general formula $CH_3C{\equiv}CCH_2OR$. Thus, for example, ethyl alcohol adds to form 4-ethoxy-2-butyne.[44] If a contact mixture of boron fluoride, mercuric oxide and trichloroacetic acid is employed, vinylacetylene readily adds three molecules of methyl alcohol, forming 2,2,4-trimethoxybutane, $CH_3O—CH_2—CH_2—C(OCH_3)_2CH_3$. The latter compound hydrolyzes to give a 75 per cent yield of 4-methoxybutan-2-one.[45]

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[35] A. S. Carter and F. B. Downing, U. S. P. 2,048,838, July 28, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 6392.

[36] British P. 438,548, 1935, to I. G. Farbenind. A. G.; *Brit. Chem. Abs.* **B**, 1936, 138. To prevent stoppage resulting from salt deposits in this type of reaction a dispersing agent, e.g., a water-soluble gum may be added to the cuprous salt solution. See R. Stadler and A. Auerhahn, German P. 639,242, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, **31**, 1431.

[37] L. G. Tzyurikh and A. A. Ginzburg, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 1468; *Chem. Abs.*, 1936, **30**, 2169.

[38] French P. 797,935, 1936, to Ammonia Casale S.A.; *Chem. Abs.*, 1936, **30**, 7121.

[39] French P. 798,309, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 7127. British P. 451,442, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, **31**, 118.

[40] L. G. Tzyurikh, E. M. Efremova, V. A. Bartashev and Yu. G. Yannu, *J. Gen. Chem.* (*U.S.S.R.*), 1936, **6**, 197; *Chem. Abs.*, 1936, **30**, 4807; *Brit. Chem. Abs.* **A**, 1936, 961.

[41] H. B. Dykstra, *J.A.C.S.*, 1934, **56**, 1625; *Chem. Abs.*, 1934, **28**, 5038; *Brit. Chem. Abs.* **A**, 1934, 990.

[42] A. S. Carter, U. S. P. 1,896,161, Feb. 7, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, **27**, 2458; *Brit. Chem. Abs.* **B**, 1933, 904. British P. 388,402, 1931; *Brit. Chem. Abs.* **B**, 1933, 379; *Chem. Abs.*, 1933, **27**, 4547. French P. 719,309, 1931; *Chem. Abs.*, 1932, **26**, 3265. N. S. Kozlov and N. P. Krechkov, Russian P. 42,073, 1935; *Chem. Abs.*, 1936, **30**, 8248.

[43] R. F. Conaway, U. S. P. 1,967,225, July 24, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 620.

[44] R. A. Jacobson, H. B. Dykstra and W. H. Carothers, *J.A.C.S.*, 1934, **56**, 1169; *Chem. Abs.*, 1934, **28**, 4373; *Brit. Chem. Abs.* **A**, 1934, 754. W. H. Carothers and R. A. Jacobson, U. S. P. 2,013,725, Sept. 10, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 6903.

Rotenberg and Favorskaya[46] have investigated the interaction of vinylacetylene with alcohols in the presence of potassium hydroxide. In the case of ethyl alcohol, the mixture, after being heated for 10 hours at 140-150°C. in an autoclave, gave a 70 per cent yield of 2-ethoxy-1,3-butadiene (b.p. 113-117°C.).

$$HC\equiv C—CH=CH_2 + C_2H_5OH \xrightarrow{KOH} CH_2=C(OC_2H_5)CH=CH_2$$

When reacted with methyl alcohol in the presence of the same alkali for 18 hours at 150°C., monovinylacetylene yielded 70 per cent of 1-methyl-1-methoxyallene (b.p., 92-100°C.).

$$HC\equiv C—CH=CH_2 + CH_3OH \xrightarrow{KOH} CH_2=C=C(OCH_3)CH_3$$

However, in the absence of the alkali hydroxide and at 100-150°C., styrene ($CH_2=CHC_6H_5$) was obtained probably as the condensation product of 2 molecules of vinylacetylene.

The addition of carboxylic acids to vinylacetylene yields esters of 1,3-butadiene-2-ol.[47] The reaction is catalyzed by a mercuric salt or by boron fluoride. For instance, 1,3-butadienyl-2-acetate may be prepared by reacting vinylacetylene with acetic acid in the presence of a mercuric sulphate-sulphoacetic acid catalyst. This ester and the corresponding formic, chloroacetic and butyric esters polymerize on standing, forming rubber-like and resinous materials.

The above-mentioned esters are analogues of chloroprene, 2-chloro-1,3-butadiene, obtained by the addition of hydrogen chloride to vinylacetylene, particularly in the presence of cuprous chloride.[48] A water-immiscible liquid, e.g., toluene, may be employed as a solvent for removing the products in this type of reaction.[49] Chloroprene is of interest because of the commercial use of its polymer, α-polychloroprene, as a synthetic rubber marketed as Neoprene.[50]

In a similar manner, hydrogen halides add to substituted monovinylacetylenes of the general formula $CH_2=CH—C\equiv C—R$ to give products analogous in character to chloroprene and capable of polymerization to rubber-like masses.[51]

Reaction of alkaline hypohalites with vinylacetylene at about 0°C. yields 1-halogeno-2-vinylacetylenes.[52] These are described as liquids with characteristic, sickening odors. Polymerization takes place on standing, forming explosive black solids. Treatment of the chloro compound, 1-chloro-2-vinylacetylene, with hydrochloric acid furnishes 1,2-dichloro-1,3-butadiene which polymerizes spontaneously to a rubber-like material.[53]

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[45] D. B. Killian, G. F. Hennion and J. A. Nieuwland, *J.A.C.S.*, 1934, **56**, 1786.

[46] I. A. Rotenberg and M. A. Favorskaya, *J. Gen. Chem. (U.S.S.R.)*, 1936, 6, 185; *Chem. Abs.*, 1936, **30**, 4808; *Brit. Chem. Abs.* **A**, 1936, 964.

[47] J. H. Werntz, *J.A.C.S.*, 1935, **57**, 204; *Chem. Abs.*, 1935, **29**, 1383; *Brit. Chem. Abs.* **A**, 1935, 472. U. S. P. 1,963,108, June 19, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 4745; *Brit. Chem. Abs.* **B**, 1935, 347. See also A. L. Klebanskii and K. K. Chevuichalova, *Sintet. Kauchuk*, **1935**, 4 (4), 5; *Chem. Abs.*, 1935, **29**, 6799.

[48] W. H. Carothers, I. Williams, A. M. Collins and J. E. Kirby, *J.A.C.S.*, 1931, **53**, 4203; *Chem. Abs.*, 1932, **26**, 78; *Brit. Chem. Abs.* **B**, 1932, 156. W. H. Carothers, G. J. Berchet and A. M. Collins, *J.A.C.S.*, 1932, **54**, 4066; *Chem. Abs.*, 1932, **26**, 5903; *Brit. Chem. Abs.* **A**, 1932, 1231. W. H. Carothers and A. M. Collins, U. S. P. 1,950,431, March 13, 1934; F. B. Downing, A. S. Carter and D. Hutton, U. S. P. 1,950,434, March 13, 1934; A. M. Collins, U. S. P. 1,950,435, March 13, 1934; *Chem. Abs.*, 1934, **28**, 3270, 3271; all patents to E. I. du Pont de Nemours & Co.

[49] G. A. Perkins, U. S. P. 2,027,550, Jan. 14, 1936, to Carbide and Carbon Chem. Corp.; *Chem. Abs.*, 1936, **30**, 1395; *Brit. Chem. Abs.* **B**, 1937, 20.

[50] The term "Neoprene" has been adopted to supplant the trade mark "Duprene" in order to provide a name which can be applied to both the unvulcanized material and to products made from it. See *Ind. Eng. Chem., News Ed.*, 1937, **15**, 43. For an extensive discussion of the preparation of chloroprene and polychloroprene and of the uses and properties of Duprene see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935, Chapter 8.

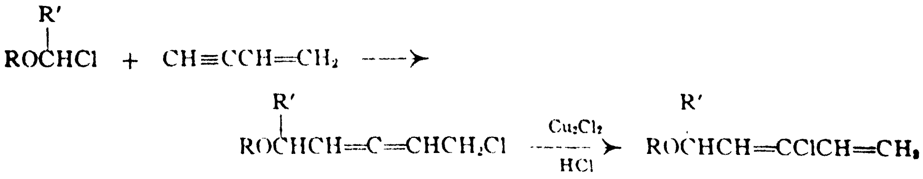
[51] R. A. Jacobson, U. S. P. 1,950,440, March 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 3270. R. A. Jacobson and W. H. Carothers, *J.A.C.S.*, 1933, **55**, 1624; *Brit. Chem. Abs.* **A**, 1933, 590; *Chem. Abs.*, 1933, **27**, 2419.

[52] R. A. Jacobson, U. S. P. 1,967,864, July 24, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 5834; *Brit. Chem. Abs.* **B**, 1935, 618. R. A. Jacobson and W. H. Carothers, *J.A.C.S.*, 1933, **55**, 4667; *Chem. Abs.*, 1934, **28**, 95; *Brit. Chem. Abs.* **A**, 1934, 55.

Dykstra[54] found that alpha chloroethers combine with vinylacetylene in a manner closely analogous to the addition of hydrogen chloride to vinylacetylene to form isochloroprene and chloroprene. A 1,4-addition (in diethyl ether) apparently takes place and is followed by isomerization in the presence of cuprous chloride and hydrochloric acid. The following general equations may represent these reactions.

Courtesy E. I. du Pont de Nemours & Co.

FIG. 153A.—Manufacture of Neoprene. At this stage the chloroprene rubber greatly resembles crude natural rubber.



$$\mathrm{RO\overset{R'}{C}HCl} + \mathrm{CH{\equiv}CCH{=}CH_2} \longrightarrow$$

$$\mathrm{RO\overset{R'}{C}HCH{=}C{=}CHCH_2Cl} \xrightarrow[\mathrm{HCl}]{\mathrm{Cu_2Cl_2}} \mathrm{RO\overset{R'}{C}HCH{=}CClCH{=}CH_2}$$

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[53] A. L. Klebanskii, A. S. Volkenshtein and A. P. Orlova, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 1255; *Chem. Abs.*, 1936, **30**, 1025.

[54] H. B. Dykstra, *J.A.C.S.*, 1936, **58**, 1747; *Chem. Abs.*, 1936, **30**, 7537.

In this way, Dykstra obtained 5-methoxy-1-chloro-2,3-pentadiene and 5-methoxy-3-chloro-1,3-pentadiene from chloromethyl methyl ether (where R is a methyl group and R′ is a hydrogen atom).

Vinylacetylene will react with Grignard reagents to form the corresponding magnesium compound, which in turn reacts with ketones, aldehydes, carboxylic acids, nitriles, isocyanates, halides and ethers to give various vinylacetylene derivatives.[55] Thus, vinylacetylene and ethylmagnesium bromide give vinylethinylmagnesium bromide, which with acetone yields vinylethinyldimethylcarbinol, $CH_2{=}CHC{\equiv}CCOH(CH_3)_2$. Compounds of this type may be synthesized also by converting vinylacetylene with alkali metals or alkali metal amides into vinylacetylides which are then treated with ketones.[56] Polymerization of vinylethinylcarbinols (accelerated by the action of air or light) yields tough or hard transparent masses which are suggested for use in coating compositions, safety glass and molding preparations.[57]

Vinylacetylene and potassium mercuri-iodide or mercuric acetate in acetic acid at room temperature form divinylethinylmercury. The latter reaction at 60-70°C. results in a 93 per cent yield of 1,1-diacetoxymercuri-2-acetoxymercurioxy-1,3-butadiene,

$$CH_2{=}CH(CH_3COOHgO)C{=}C(HgOOCCH_3)_2.$$

which is decomposed by hydrochloric acid to methyl vinyl ketone.[58] By leading vinylacetylene into an acid solution of a mercuric salt (e.g., mercuric sulphate in sulphuric acid) and subsequently decomposing the resultant mercury compound with hydrochloric acid at 90-100°C. biacetyl is produced.[59] Utilization of the latter compound as a flavoring agent in butter substitutes has been suggested.[60] Monovinylacetylene in compressed or liquid form has been proposed as a combustion gas for such industrial purposes as welding, heating and illumination.[61]

Divinylacetylene. As mentioned previously, divinylacetylene is formed by the same methods employed for monovinylacetylene, the divinyl compound being a trimer of acetylene whereas monovinylacetylene is the dimer.[62] The trimer is quite unstable; on exposure to air it is transformed into a dangerously explosive, soft jelly-like mass. The pure compound decomposes at 105-110°C., but below this temperature it is capable of polymerizing in an inert atmosphere to yellow, viscous liquids or hard, insoluble resins.[63] Because of the ability of these viscous liquids to polymerize further to form hard, chemically resistant films they have been employed as synthetic drying oils.[64] Partial hydrogenation of divinylacetylene before polymerization is said to increase the stability of its polymers to light.[65] From the oily polymers, Cupery and Carothers[66] isolated a dimer, trans-1,2-bis(vinylethinyl)cyclobutane,

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[55] W. H. Carothers and G. J. Berchet, *J.A.C.S.*, 1933, **55**, 1094; *Brit. Chem. Abs.* **A**, 1933, 485; *Chem. Abs.*, 1933, **27**, 1860. U. S. P. 1,963,935, June 19, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 347; *Chem. Abs.*, 1934, **28**, 5081. French P. 753,465, 1933; *Chem. Abs.*, 1934, **28**, 1051. See also Y. S. Zalkind and V. M. Pletz, *Trans. Leningrad Chem.-Tech. Inst.*, 1934, 1, 57; *J. Gen. Chem.* (*U.S.S.R.*), 1934, **4**, 1088; *Chem. Abs.*, 1935, **29**, 2908.

[56] W. H. Carothers and R. A. Jacobson, *J.A.C.S.*, 1933, **55**, 1097; *Chem. Abs.*, 1933, **27**, 1860; *Brit. Chem. Abs.* **A**, 1933, 485. U. S. P. 1,963,934, June 19, 1934, to E. I du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 5081; *Brit. Chem. Abs.* **B**, 1935, 347. French P. 753,465, 1933; *Chem. Abs.*, 1934, **28**, 1051.

[57] W. H. Carothers, G. J. Berchet and R. A. Jacobson, U. S. P. 1,963,074, June 19, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 4848.

[58] W. H. Carothers, R. A. Jacobson and G. J. Berchet, *J.A.C.S.*, 1933, **55**, 4665.

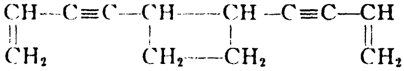
[59] E. Eberhardt, U. S. P. 2,062,263, Nov. 24, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, **31**, 711. British P. 421,676, 1934; *Brit. Chem. Abs* **B**, 1935, 218; *Chem. Abs.*, 1935, **29**, 3692. French P. 776,584, 1935; *Chem. Abs.*, 1935, **29**, 3354.

[60] See G. Benson and A. F. G. Cadenhead, *J.S.C.I.*, 1934, **53**, 42T; *Chem. Abs.*, 1934, **28**, 2321; *Brit. Chem. Abs.* **B**, 1934, 265. O. Gebhardt, *Seifensieder Ztg.*, 1934, **61**, 113, 131; *Chem. Abs.*, 1934, **28**, 3144. W. L. Davies, *Food Manuf.*, 1933, **8**, 346; *Chem. Abs.*, 1934, **28**, 835. B. W. Hammer, *Proc. 7th Ann. State Coll. Washington Inst. Dairying*, **1934**, 16; *Chem. Abs.*, 1934, **28**, 6658.

[61] French P. 789,174, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 1981. British P. 439,689, 1935; *Chem. Abs.*, 1936 **30**, 3624.

[62] Acetylenebivinyl, $CH_2{=}CHCH{=}CHC{\equiv}CH$, another trimer of acetylene, has been obtained by A. K. Klebanskii, U. A. Dranitzina and I. M. Dobromilskaya, *Compt. rend. acad. sci. U.R.S.S.*, 1935, 2, 229; *Chem. Abs.*, 1935, **29**, 6205.

[63] J. A. Nieuwland, W. S. Calcott, F. B. Downing and W. H. Carothers, *J.A.C.S.*, 1931, **53**, 4197; *Chem. Abs.*, 1932, **26**, 78; *Brit. Chem. Abs.* **A**, 1932, 40. See also W. S. Calcott and F. B. Downing, U. S. P. 1,924,979, Aug. 29, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.* 1931, **25**, 5341. German P. 601,504, 1933; *Chem. Abs.*, 1934, **28**, 7264.



The presence of a trimer, a bis(vinylethinylcyclobutyl)acetylene in the oily mixture was postulated.

Chlorine reacts with divinylacetylene by 1,4 addition to yield a dichloride and then a tetra- and hexachloride.[67] By the action of hydrochloric acid at room temperature a dihydrochloride, 1,3-dichloro-2,4-hexadiene is formed.[68] In both of these reactions all unsaturated linkages are involved. Combination with thio-*p*-cresol, however, involves only the ethylene linkages, giving rise to 1,6-bis(*p*-tolylthio)-3-hexine.[69] Hydration of divinylacetylene furnishes vinyl allyl ketone (b.p. 85-86°C. at 20 mm.) an oily liquid with a sharp odor.[70] Treatment of divinylacetylene with a hydrogen polysulphide at temperatures of —10 to 10°C. is said to give resinous materials applicable as paint and lacquer vehicles.[71] Products of a resinous or viscous oily nature, which in air dry to resistant films, may be procured by simultaneous reaction of hydrogen sulphide and sulphur with mono- or divinylacetylene in the presence of a catalyst of dibutylamine, aniline or pyridine.[72]

HALOGEN DERIVATIVES OF ACETYLENE

Of the various halogen derivatives of acetylene, those containing chlorine are the most important. The ultimate product of the chlorination of acetylene is acetylene tetrachloride (tetrachloroethane) from which several chlorinated solvents, particularly trichloroethylene, $CHCl=CCl_2$, can be made.

Continuous production of acetylene tetrachloride in 95-98.5 per cent yield has been described by Favorskii, Margules and Davuidova.[73] Dry acetylene and chlorine are fed into the top of a jacketed iron column completely filled with iron shavings. Acetylene tetrachloride is sprayed in under pressure, and this, plus an additional amount formed in the reaction, drips into a receiver filled with pebbles to facilitate the trapping of gases. Temperatures of 60-70°C. were recommended. A 90 per cent yield is said to be possible at 70-75°C. but at 100°C. considerable hexachloroethane is formed.[74]

Chlorination of acetylene-hydrogen mixtures (e.g., from decomposition of methane) to acetylene tetrachloride, $CHCl_2CHCl_2$, has been carried out at 100-

[64] See O. M. Hayden, *Ind. Eng. Chem.*, 1932, **24**, 563; *Chem. Abs.*, 1933, **27**, 3091; *Brit. Chem. Abs.* **B**, 1932, 649. Also, Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**, Chapter 8.

[65] W. S. Calcott, A. S. Carter and F. B. Downing, U. S. P. 1,959,343 and 1,959,408, May 22, 1934, to E. I. du Pont de Nemours & Co ; *Chem. Abs.*, 1934, **28**, 4434, 4615.

[66] M. E. Cupery and W. H. Carothers, *J.A.C.S*, 1934, **56**, 1167.

[67] D. D. Coffman and W. H. Carothers, *J.A.C.S.*, 1933, **55**, 2040.

[68] D. D. Coffman, J. A. Nieuwland and W. H. Carothers, *J.A.C.S.*, 1933, **55**, 2048; *Chem. Abs.*, 1933, **27**, 2933; *Brit. Chem. Abs.* **A**, 1933, 694.

[69] W. H. Carothers, *J.A.C.S.*, 1933, **55**, 2008.

[70] P. V. Zhavornokov, A. P. Alekhina and R S. Shter, *Sintet Kauchuk*, **1934** (2), 12; *Chem. Abs.*, 1935, **29**, 3976.

[71] W. H. Carothers, U. S. P. 2,061,018, Nov. 17, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, **31**, 781.

[72] A. S. Carter and F. B. Downing, U. S. P. 2,061,019, Nov. 17, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, **31**, 781.

[73] A. E. Favorskii, E. Z. Margules and M. I. Davuidova, *Trans. State Inst. Appl. Chem.* (*U.S.S.R.*), 1935, **24**, 47; *Chem. Abs.*, 1935, **29**, 7271.

[74] I. F. Suknevich and M. S. Khomutin, *Trans. State Inst. Appl. Chem.* (*U.S.S.R.*), 1935, **24**, **54**; *Chem. Abs.*, 1935, **29**, 7271.

200°C. using as catalysts iron compounds on a carrier of silicates or silica gel.[75] It is stated that formation of hydrogen chloride is avoided in the chlorination of cracked gases containing acetylene if temperatures of 80-140°C. are employed.[76]

On dechlorination by various means, e.g., by action of alkalies or by catalytic decomposition, acetylene tetrachloride is converted into trichloroethylene.[77] Because of its powerful solvent action, low surface tension and high penetration, this trichloro derivative has found a number of uses.[78] For instance, it has been employed as an extracting agent in the winning of vegetable oils, e.g., soya bean oil,[79] and in the decaffeination of coffee beans.[80] Its high specific gravity (1.47) and low specific heat and heat of vaporization have made trichloroethylene useful in dewaxing petroleum oils by centrifugal means.[81] This compound has also been employed as a constituent of insecticidal sprays[82] and polishes for floors, furniture, boots and shoes,[83] and a grease solvent in the cleaning of metal pipes.[84]

Because of the varied applications of trichloroethylene, its stability and corrosive action are of interest. Carlisle and Levine[85] state that it is not corrosive if antioxidants are present and that even in their absence action is only slight.[86] The compound is quite stable to light unless oxygen is present. Decomposition by action of light is also prevented by the addition of antioxidants. Among the substances proposed as stabilizers for trichloroethylene are alkylamines and benzylamines, diphenylguanidine,[87] triethylamine,[88] amylene,[89] mercaptans,[90] phenolic substances[91] and caffeine.[92] The toxicity of trichloroethylene has been noted by many workers[93] although in some cases the compound has served as an anesthetic.[94] Mercury trichloroethylenide may be prepared by agitating trichloroethylene with an aqueous alkaline solution of an alkali metal cyanide to which a paste of freshly precipitated mercuric oxide has been added.[95]

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[75] H. Tramm, U. S. P. 2,016,658, Oct. 8, 1935, to Ruhrchemie A.-G.; *Chem. Abs.*, 1935, **29**, 8005. O. Klein, German P. 613,607, 1935, to Ruhrchemie A.-G.; *Chem. Abs.*, 1935, **29**, 8007.

[76] P. Baumann, R. Stadler and E. Willig, U. S. P. 2,016,572, Oct. 8, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 8005. British P. 397,961, 1933; *Brit. Chem. Abs.* **B**, 1933, 954; *Chem. Abs.*, 1934, **28**, 1052. German P. 606,694, 1934, *Chem. Abs.*, 1935, **29**, 3691; *J. Inst. Pet. Tech.*, 1935, **21**, 141A. French P. 739,183, 1932; *Chem. Abs.*, 1933, **27**, 1894.

[77] Several methods of dechlorination are mentioned by Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, **1934**, 673. For the use of active carbon in dechlorination see S. Yamaguchi, *J. Chem. Soc. Japan*, 1934, **55**, 1227; *Chem. Abs.*, 1935, **29**, 4326.

[78] See S. Wernick, *Ind. Chemist*, 1934, **10**, 479; *Brit. Chem. Abs.* **B**, 1935, 154; *Chem. Abs.*, 1935, **29**, 5403. Also, *Ind. Chemist*, 1933, **9**, 349; *J. Inst. Pet. Tech.*, 1934, **20**, 186A. For methods of detecting trichloroethylene, see H. H. Weber, *Chem.-Ztg.*, 1933, **57**, 836; *Brit. Chem. Abs.* **B**, 1933, 1046; *Chem. Abs.*, 1934, **28**, 727. A. Gruning and M. Schnetka, *Arch. Gewerbepath. Gewerbehyg.*, 1933, **4**, 740; *Chem. Abs.*, 1934, **28**, 991; *Brit. Chem. Abs.* **B**, 1934, 311; *Chem. Zentr.*, 1935, **1**, 3961.

[79] M. Nakamura, Japanese P. 109,730, 1935, addn. to 107,890, to Honen Seiyu K. K.; *Chem. Abs.*, 1935, **29**, 4962.

[80] H. K. Wilder, U. S. P. 1,977,416, Oct. 16, 1934, to Kellogg Co.; *Chem. Abs.*, 1935, **29**, 249; *Brit. Chem. Abs.* **B**, 1935, 923.

[81] N. O. Backlund, *J. Inst. Pet. Tech.*, 1933, **19**, 1. See also *Chem. Fabrik*, 1934, **7**, 355. British P. 435,648, 1934, to Aktiebolaget Separator-Nobel; *Brit. Chem. Abs.* **B**, 1935, 1127; *Chem. Abs.*, 1936, **30**, 1553. German P. 610,807, 1935; *Chem. Abs.*, 1935, **29**, 6043. French P. 778,880, 1935; *Chem. Abs.*, 1935, **29**, 4931. For use of a mixture of propane and trichloroethylene see U. B. Bray, U. S. P. 2,031,096, Feb. 18, 1936, to Union Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 2364.

[82] G. Algard, British P. 440,536, 1936; *Chem. Abs.*, 1936, **30**, 3936; *Brit. Chem. Abs.* **B**, 1936, 302.

[83] H. Deguide, British P. 438,841, 1935; *Chem. Abs.*, 1936, **30**, 3134.

[84] E. W. Johnson and R. A. Eastwood, British P. 427,753, 1935, to Imperial Chemical Industries Ltd.; *Chem. Abs.*, 1935, **29**, 6335. For a review of the use of trichloroethylene as a solvent for grease removal from metals, see M. Damien, *Métaux, Aciers spéciaux*, 1934, **9**, 591; *Brit. Chem. Abs.* **B**, 1936, **30**, 7518.

[85] P. J. Carlisle and A. A. Levine, *Ind. Eng. Chem.*, 1932, **24**, 1164.

[86] Some investigators disagree. See, for example, S. S. Drozdov and N. S. Drozdov, *J. Chem. Ind. (Moscow)*, 1934, **10** (2), 53; *Chem. Abs.*, 1934, **28**, 3704.

[87] *Chem. Trade J.*, 1933, **93**, 227; *Chem. Abs.*, 1934, **28**, 4026; *Brit. Chem. Abs.* **B**, 1933, 969.

[88] A. L. Pitman, U. S. P. 1,925,602, Sept. 5, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1934, 617.

[89] C. R. Harris, U. S. P. 1,904,450; April 18, 1933, to Roessler and Hasslacher Chem. Co.; *Chem. Abs.*, 1933, **27**, 3481. German P. 562,820, 1933; *Chem. Abs.*, 1933, **27**, 992.

[90] L. C. Stewart and L. DePree, U. S. P. 1,917,073, July 4, 1933, to Dow Chem. Co.; *Chem. Abs.*, 1933, **27**, 4539.

[91] P. J. Carlisle and C. R. Harris, U. S. P. 2,008,680, July 23, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 5855. Canadian P. 341,792, 1934; *Chem. Abs.*, 1934, **28**, 5076.

[92] P. J. Carlisle, U. S. P. 1,996,717, April 2, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 3353.

[93] M. E. van Themsche, *Ing. chim.*, 1934, **18**, 58; *Chem. Abs.*, 1934, **28**, 7360. H. Persson, *Acta Med. Scand.*, 1934, **59** (Suppl.), 410; *Chem. Abs.*, 1935, **29**, 3041. C. Vallee and J. Leclerq, *Ann. med. legale criminol. police sci.*, 1935, **15**, 10; *Chem. Abs.*, 1935, **29**, 4695.

In addition to its possible use as an anesthetic, trichloroethylene has also been suggested as a remedy for migraine (severe headache). Geiger and Goodman,[95a] however, relate they did not obtain favorable results with this halogenated olefin, as only a small proportion of patients treated experienced relief.

It is reported that trichloroethylene heated with metals such as zinc, iron and cadmium in the presence of water yields dichloroethylene.[96] Conversion of either geometrical isomer of 1,2-dichloroethylene into the other is said to occur on treatment with a small proportion of bromine in the presence of antimony bromide.[97]

The photobromination of acetylene at 150°C. yields dibromoethylene, according to Booher and Rollefson.[98] To produce *sym*-tetrabromoethane, acetylene may be led into aqueous solutions containing bromides to which chlorine water has been added to form free bromine.[99]

Although many investigators have reported that very little or no action takes place in the cold between acetylene and iodine, Ellis[100] noted that almost complete conversion to acetylene diiodide ($C_2H_2I_2$, diiodoethylene) was effected in 2-3 days at 25°C. in a container whose inside surface was coated with sublimed iodine. Previous workers[101] found that reaction of acetylene with iodine (most favorably at 140-160°C.) gives a mixture of two isomeric 1,2-diiodoethylenes. Kaufmann[102] has stated that the action of metallic sodium on 1,2-diiodoethylene (acetylene iodide) in ether solution causes the formation of 1,1-diiodoethylene. This statement was refuted by Emschwiller[103] who believed that such a reaction resulted in a 30 per cent conversion to diiodoacetylene, $CI{\equiv}CI$, the remainder being unchanged diiodoethylene. Vaughn and Nieuwland[104] obtained diiodoacetylene by iodination of acetylene or of sodium acetylide in liquid ammonia. Dehn[105] prepared the same compound by action of sodium hypoiodite (from sodium hypochlorite and potassium iodide) on acetylene. Reaction of iodine with sodium acetylide in benzene has yielded triiodoethylene and tetraiodoethylene.[106] Mono- and diiodoacetylene may be formed by the action of iodo-silver benzoate on acetylene.[107]

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[94] H. L. Tschenke, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 21; *Chem. Abs.*, 1934, **28**, 1138; *Brit. Chem. Abs.* **B**, 1934, 300. D. E. Jackson, *Anesthesia and Analgesia*, 1934, **13**, 198; *Chem. Abs.*, 1935, **29**, 1501. J. C. Krantz, C. J. Karr and R. Musser, *J. Am. Pharm. Assoc.*, 1935, **24**, 754; *Chem. Abs.*, 1935, **29**, 8233. H. Taylor, *J. Ind. Hyg. Toxicol.*, 1936, **18**, 175; *Chem. Abs.*, 1936, **30**, 3881.

[95] H. E. Parker, British P. 427,979, 1935, to Imperial Chemical Industries Ltd.; *Chem. Abs.*, 1935, **29**, 6608.

[95a] A. J. Geiger and L. S. Goodman, *J. Amer. Med. Assoc.*, 1937, **108**, 1733.

[96] British P. 436,133, 1935, to Compagnie de prod. chim. et electromet. Alais, Froges et Camargue; *Chem. Abs.*, 1936, **30**, 1394; *Brit. Chem. Abs.* **B**, 1935, 1129. French P. 786,803, 1935; *Chem. Abs.*, 1936, **30**, 737.

[97] M. Mugdan and T. Rost, German P. 595,464, 1934, to Consortium für elektrochem. industrie; *Chem. Abs.*, 1934, **28**, 4072.

[98] J. E. Booher and G. K. Rollefson, *J.A.C.S.*, 1934, **56**, 2288; *Chem. Abs.*, 1935, **29**, 405; *Brit. Chem. Abs.* **A**, 1935, 48. See also W. Franke and H. J. Schumacher, *Z. physik. Chem.*, 1936, **B34**, 181; *Chem. Abs.*, 1937, **31**, 1298.

[99] B. T. Pavlov and M. D. Ryazantzev, Russian P. 33,535, 1933; *Chem. Abs.*, 1934, **28**, 3424.

[100] C. P. Ellis, *J.C.S.*, **1934**, 726.

[101] E. Paterno and A. Peratoner, *Gazz. chim. ital.*, 1889, **19**, 580; *J.C.S.*, 1890, **58**, 1219. E. H. Keiser, *Am. Chem. J.*, 1899, **21**, 261; *J.C.S.*, 1899, **76** (1), 398. G. Chavanne and J. Vos, *Compt. rend.*, 1914, **158**, 1582; *Chem. Abs.*, 1914, **8**, 3010. A. Sabanajeff, *Ann.*, 1875, **178**, 109; *J.C.S.*, 1876, **29**, 55.

[102] H. P. Kaufmann, *Ber.*, 1922, **55**, 249; *J.C.S.*, 1922, **122** (1), 213.

[103] G. Emschwiller, *Bull. soc. chim.*, 1935, (5) **2**, 1625; *Chem. Abs.*, 1936, **30**, 429. See also *Compt. rend.*, 1934, **198**, 1151; *Chem. Abs.*, 1934, **28**, 3000.

[104] T. H. Vaughn and J. A. Nieuwland, *J.A.C.S.*, 1932, **54**, 787; 1933, **55**, 2150; *Chem. Abs.*, 1932, **26**, 1573; 1933, **27**, 2933; *Brit. Chem. Abs.* **A**, 1932, 362; **A**, 1933, 694.

[105] W. H. Dehn, *J.A.C.S.*, 1911, **33**, 1598; *Chem. Abs.*, 1911, **5**, 3802; *J.C.S.*, 1911, **100** (1), 914.

[106] M. Skosarewski, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 863; *J.C.S.*, 1904, **86** (1), 793. H. Moissan, *Compt. rend.*, 1898, **127**, 914; *J.C.S.*, 1899, **76** (1), 241.

[107] C. Prevost, *Compt. rend.*, 1935, **200**, 942; *Brit. Chem. Abs.* **A**, 1935, 728.

HYDRATION OF ACETYLENE TO ACETALDEHYDE

Of the many chemical reactions of acetylene perhaps the most important is its hydration to acetaldehyde. The latter can then be employed in the manufacture of acetone, acetic acid, crotonaldehyde, ethanol, butanol, butyric acid and ethyl acetate as well as many other products, including synthetic resins.[108]

The usual industrial method for hydration of acetylene consists in conducting the gas through an acid solution containing a catalyst. One procedure has been described by Thommen.[109] A large excess of acetylene is passed continuously through an apparatus filled with 30 per cent sulphuric acid maintained at 60-70°C. A steady stream of mercuric oxide suspended in water is fed into the acid, which is kept well agitated. Water vapor and the acetaldehyde formed are carried along with the gas stream which is run through condensers and washers to remove acetaldehyde. Unreacted acetylene is then returned to the reaction vessel to repeat the cycle. The aldehyde water from the washers contains 10-20 per cent of acetaldehyde, which is recovered by rectification. Sludge formation and consumption of mercuric oxide are minimized by use of purified acetylene.

A number of catalysts have been proposed for the hydration of acetylene in both the liquid and gaseous phases.[110] Millar and Steck[111] suggested a solution containing a free acid, a mercury compound and an acid salt of an alkali metal or of ammonia. Rosinsky and Baumann[112] have passed acetylene into concentrated aqueous solutions of normal salts with acid reaction, e.g., the halides of zinc, chromium, cadmium, iron, magnesium and calcium. Yields are said to be increased by the use of promoters, e.g., mercury compounds and water-soluble salts of uranium, gold and platinum. For vapor-phase hydration, acetylene and water vapor may be passed over tungstic oxide or sulphide, tungstic acid or ammonium tungstate at 300-400°C. Activators, such as zinc oxide or selenide, copper oxide and cobalt sulphide may be incorporated with the catalyst.[113] For this type of hydration, aluminum oxide may be employed, with oxides or sulphides of cadmium and zinc or with chromates, tungstates or molybdates as dehydrogenating catalysts.[114] Also, the use of a mixture of phosphates of cadmium and an alkaline earth metal (e.g., calcium) has been proposed, temperatures of 250-400°C. being employed.[115]

Catalytic hydration of acetylene may also be carried out in two stages, the first in liquid phase and the second in gaseous phase.[116] In the first stage, a portion of the hydrocarbon is converted to acetaldehyde by passing through an acid (for example, sulphuric acid) containing mercury, usually as mercurous sulphate. The unchanged acetylene is converted in the gaseous phase by catalytic reaction with steam.[117] To make acetaldehyde distillation-stable in monomeric or trimeric form it may be treated with acid-binding substances, e.g., sodium acetate.[118]

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[108] See Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[109] H. Thommen, *Chem.-Ztg.*, 1934, **58**, 797; *J. Inst. Pet. Tech.*, 1935, **21**, 22A

[110] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934, 676.

[111] R. W. Millar and L. V. Steck, U. S. P. 2,005,946, June 25, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 5461; *Brit. Chem. Abs.* **B**, 1936, 824. Canadian P. 337,706, 1933; *Chem. Abs.*, 1934, **28**, 1720.

[112] W. Rosinsky and P. Baumann, German P. 621,292, 1935, addn. to 620,402, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 737, 1071. British P. 393,690, 1933, addn. to 313,864, 1928; *Chem. Abs.*, 1930, **24**, 1125; 1933, **27**, 5751; *Brit. Chem. Abs.* **B**, 1929, 708; **B**, 1933, 822.

[113] British P. 329,867, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, **24**, 5768.

[114] British P. 332,635, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, **24**, 304.

[115] A. Scheuermann, R. Brill and G. Wietzel, German P. 637,186, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, **31**, 711. British P. 452,527, 1936; *Brit. Chem. Abs.* **B**, 1936, 1142; *Chem. Abs.*, 1937, **31**, 1045. See also H. Dreyfus, U. S. P. 2,045,841, June 30, 1936; *Chem. Abs.*, 1936, **30**, 5597.

[116] British P. 425,069, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 5128; *Brit. Chem. Abs.* **B**, 1935, 620. French P. 776,518, 1935; *Chem. Abs.*, 1935, **29**, 3354.

Although acetic acid can be made from acetaldehyde by oxidation,[119] numerous methods have been proposed for its manufacture directly from acetylene.[120] In one such procedure a mixture of acetylene, water vapor and oxygen is saturated with mercury vapor and passed over a porous body carrying a hydration catalyst, e.g., phosphoric acid and zinc oxide, or ferric hydroxide or vanadium oxide. By using active carbon and mercuric phosphate a yield of 60 per cent acetic acid and 14 per cent acetaldehyde has been reported.[121] Acetaldehyde, acetone and acetic acid

Courtesy E. I. du Pont de Nemours & Co.

FIG. 153B.—Acetylene Generators Employed in Manufacture of Neoprene.

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[117] British P. 448,871, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 7587; *Brit. Chem. Abs.* **B**, 1936, 824.

[118] H. Deutsch and W. O. Herrmann, German P. 617,762, 1935, to Chem. Forschungs G.m.b.H.; *Chem. Abs.*, 1936, **30**, 736.

[119] See, e.g., K. Wiesler, U. S. P. 1,953,381, April 3, 1934, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1934, **28**, 3743.

[120] *Cf.*, S. N. Kazarnovskii and A. B. Feigin, *J. Chem. Ind.* (*Moscow*), 1935, **12**, 150; *Chem. Abs.*, 1935, **29**, 5813. Y. Mayor, *Rev. chim. ind.* (*Paris*), 1936, **45**, 302; *Chem. Abs.*, 1937, **31**, 1763.

[121] E. Eberhardt, U. S. P. 1,972,476, Sept. 4, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 6446. German P. 544,691, 1930 and addn. 554,784, 1930; *Chem. Abs.*, 1932, **26**, 3521, 5971. British P. 364,255, 1932; *Brit. Chem. Abs.* **B**, 1932, 459.

may be obtained by conducting acetylene and steam at 300-450°C. through a fused salt with acid reaction. A mixture of zinc chloride and aluminum chloride may be employed.[122] Catalysts for the reaction include the oxides of cerium, chromium, barium, zinc and titanium mixed with potassium hydroxide or sodium silicate.

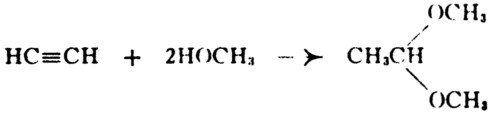
Under proper conditions, acetone may be synthesized from acetylene and steam or from acetaldehyde and steam. For example, reaction between acetylene and water vapor to form acetone may take place at 250-700°C. under 3-10 atmospheres pressure, and catalyzed by oxides of iron, manganese, cobalt, thorium, cerium or tin, or dusty iron sponge impregnated with iron and manganese acetates.[123] Roka and Wiesler[124] suggest reaction of one part acetylene with 5 to 15 parts steam at 300-600°C. in contact with a mixture of oxides having a partial pressure of oxygen within the range 10^{-25} to 10^{-32} atmospheres.

Zelinski and co-workers[125] investigated the use of an iron-manganese catalyst in the synthesis of acetone. With a composition consisting of 7 parts ferric oxide and 3 parts manganese dioxide, acetaldehyde and steam at 400-440°C. gave a 96 per cent yield of acetone. On the other hand, a yield of 88 per cent was obtained with acetylene and steam although this could be raised to 98 per cent by passing the reacting gases over the contact agent a second time. Acetone in 89 per cent yield has been reported from the reaction of acetylene and steam at 450°C. with a catalyst of 4 parts zinc oxide and one part manganous oxide.[126] A possible mechanism for the above reactions is, acetylene first reacts with water to form acetic acid, which then is converted into acetone.[127]

According to Walter,[128] acetone may be synthesized by passing a mixture of acetylene and steam over active carbon impregnated with barium and zinc compounds at 400°C. or with zinc and calcium compounds at 500°C. Yields of 90 per cent are reported.

CONDENSATION OF ACETYLENE WITH HYDROXY COMPOUNDS

By use of catalysts, acetylene may be condensed with alcohols and related hydroxy compounds to form acetals. Thus, methanol reacts with acetylene in the presence of mercuric chloride to form dimethyl acetal.[129]



$$HC{\equiv}CH + 2HOCH_3 \longrightarrow CH_3CH(OCH_3)_2$$

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[122] H. Deutsch and W. O. Herrmann, German P. 583,975, 1933, to Consortium für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1934, **28**, 1058. British P. 373,893, 1931; *Brit. Chem. Abs.* **B**, 1932, 832; *Chem. Abs.*, 1933, **27**, 3951. French P. 722,190, 1931; *Chem. Abs.*, 1932, **26**, 4067.

[123] W. Pohl, U. S. P. 1,953,499, April 3, 1934, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1934, **28**, 3744; *Brit. Chem. Abs.* **B**, 1935, 139. German P. 567,118, 1930; *Chem. Abs.*, 1933, **27**, 1365.

[124] K. Roka and K. Wiesler, U. S. P. 2,014,294, Sept. 10, 1935; *Chem. Abs.*, 1935, **29**, 7346. German P. 565,944, 1926, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1933, **27**, 2459.

[125] N. D. Zelinskii, M. I. Ushakov, B. M. Mikhailov and J. A. Arbuzov, *J. Applied Chem.* (*U.S.S.R.*), 1934, **7**, 83; *Brit. Chem. Abs.* **B**, 1934, 567; *Chem. Abs.*, 1934, **28**, 7245; *J. Chem. Ind.* (*Moscow*), **1933** (7), 63; *Chem. Abs.*, 1934, **28**, 1015; *Brit. Chem. Abs.* **B**, 1934, 52.

[126] M. I. Ushakov and M. I. Rozengart, *J. Chem. Ind.* (*Moscow*), **1934** (4), 66; *Chem. Abs.*, 1934, **28**, 4698; *Brit. Chem. Abs.* **B**, 1934, 792. Various catalysts have been investigated by M. S. Platonov, V. A. Plakidina and K. K. Veltistov, *J. Gen. Chem.* (*U.S.S.R.*), 1934, **4**, 421; *Chem. Abs.*, 1935, **29**, 1774; *Brit. Chem. Abs.* **A**, 1934, 1336.

[127] For a study of the mechanism of this reaction, see M. Ya. Kagan, I. A. Sobolev and G. D. Lyubarski, *Ber.*, 1935, **68**, 1140; *Chem. Abs.*, 1935, **29**, 6207; *Brit. Chem. Abs.* **A**, 1935, 963.

[128] H. Walter, German P. 584,517, 1933, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1934, **28**, 1058.

[129] J. S. Reichert, J. H. Bailey and J. A. Nieuwland, *J.A.C.S.*, 1923, **45**, 1552; *Chem. Abs.*, 1923, **17**, 2413; *J.C.S.*, 1923, **124** (1), 753. A study of this reaction is made by S. Tamaru and Y. Tanaka, *J. Chem. Soc. Japan*, 1935, **56**, 486; *Chem. Abs.*, 1935, **29**, 4733; *Brit. Chem. Abs.* **A**, 1936, 453.

Cyclic acetals result when polyhydric alcohols are substituted for monohydric and mercuric sulphate and concentrated sulphuric acid used as catalyst.[130] It is reported that by this method good yields of cyclic ethylidene derivatives of ethylene glycol, trimethylene glycol, propene glycol, 1,4-tetramethylene glycol, glycerol, glycerol-α-bromohydrin, pinacol and α-methyl glucoside have been obtained. In order to reduce tar formation, Mitchell[131] employed acid-free, freshly precipitated mercuric sulphate. Another catalyst proposed is a mixture of a mercuric compound and fluoboric or fluosilicic acid.[132]

Resinous products result from the condensation of phenol or cresols with acetylene.[133] With β-naphthol, an acetal together with some ethylidene di-β-naphthol is secured. Reaction of acetylene with resorcinol is said to give first vinylresorcinol and then ethylidene diresorcinol. The latter loses water to form dihydroxymethylxanthene, which on oxidation yields hydroxymethylfluorene.[134]

Acetals, on treatment with the proper catalysts, yield unsaturated ethers. For example, acetal vapors may be led at 200-350°C. over finely divided gold, silver, platinum or palladium mixed with auxiliary agents, e.g., copper, aluminum, calcium, zinc, thorium, tungsten, manganese or their oxides, phosphates or silicates.[135] By the reverse reaction, combination of unsaturated ethers with alcohols, acetals may be formed.[136] Vinyl ethers are of interest because of their tendency to polymerize to resinous materials useful in such products as adhesives and lacquers.[137] Divinyl ether, prepared by the action of potassium hydroxide on β,β'-dichloroethyl ether, is used to some extent as an anesthetic.[138]

Reppe[139] has produced vinyl ethers by the action of acetylene on monomeric hydroxy compounds at 80-250°C. in the presence of alkaline catalysts. For example, *n*-butanol and acetylene (potassium hydroxide as catalyst) at 150°C. furnish vinyl butyl ether in 95 per cent yield.[140] Likewise ethylene glycol and acetylene at 120°C. give 33 per cent of ethylene glycol monovinyl ether, 10 per cent of ethylene glycol divinyl ether and 50 per cent of unchanged glycol. In an analogous manner mercaptans unite with acetylene to form vinyl thioethers.[141] Vinyl phenyl ether may be prepared in the vapor phase at about 270°C. from acetylene and phenol, employing a zinc or cadmium salt, e.g., zinc acetate, as catalyst.[142] Vinyl ethers of aromatic hydroxyalkylamines are formed by reaction of the latter with acetylene, using alkaline catalysts.[143]

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[130] H. S. Hill and H. Hibbert, *J.A.C.S.*, 1923, **45**, 3108; *J.C.S.*, 1924, **126** (1), 133; *Chem. Abs.*, 1924, **18**, 1987. See also H. Walter, British P. 288,707, 1927, to Verein für Chem. Ind. A.-G.; *Chem. Abs.*, 1929, **23**, 607; *Brit. Chem. Abs.* **B**, 1928, 440.

[131] W. Mitchell, British P. 428,080, 1935, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1935, **29**, 6608.

[132] British P. 384,332, 1932, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1933, 181.

[133] See Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**, Chapter 18. See also, e.g., W. Reppe and E. Keyssner, U. S. P. 2,027,199, Jan. 7, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 1468. French P. 758,042, 1934, and addn. 44,008, 1934; *Chem. Abs.*, 1934, **28**, 3255; 1935, **29**, 3073.

[134] H. H. Wenzke and J. A. Nieuwland, *J.A.C.S.*, 1924, **46**, 177; *Chem. Abs.*, 1924, **18**, 1995; *J.C.S.*, 1924, **126** (1), 282. S. A. Flood and J. A. Nieuwland, *J.A.C.S.*, 1928, **50**, 2566; *Brit. Chem. Abs.* **A**, 1928, 1239; *Chem. Abs.*, 1928, **22**, 3643.

[135] K. Baur, U. S. P. 1,931,858, Oct. 24, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 485. British P. 345,253, 1929; *Chem. Abs.*, 1932, **26**, 156.

[136] W. Reppe and K. Baur, U. S. P. 2,000,252, May 7, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 4029. British P. 352,474, 1930; *Brit. Chem. Abs.* **B**, 1931, 1040.

[137] For a more complete treatment of this subject see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**, Chapter 50.

[138] See Chapter 21. *Cf.* Chapter 53 on the use of petroleum hydrocarbons in anesthesia.

[139] W. Reppe, U. S. P. 1,959,927, May 22, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 4431. German P. 584,840, 1933; *Chem. Abs.*, 1934, **28**, 1058. British P. 369,297, 1932 and addn. 430,764, 1935; *Brit. Chem. Abs.* **B**, 1932, 670; 1935, 795; *Chem. Abs.*, 1933, **27**, 2159; 1935, **29**, 8001. French P. 724,955, 1931; *Chem. Abs.*, 1932, **26**, 4825.

[140] This reaction may also take place in the vapor phase at 250-300°C. W. Reppe and W. Wolff, U. S. P. 2,066,076, Dec. 29, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, **31**, 1037. British P. 427,036, 1935, addn. to 369,297, 1932; *Chem. Abs.*, 1935, **29**, 6247; *Brit. Chem. Abs.* **B**, 1935, 584. French P. 45,333, 1935, addn. to 724,955, 1931; *Chem. Abs.*, 1936, **30**, 2578.

[141] W. Reppe and F. Nicolai, German P. 617,543, 1935, and 624,845, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 733, 4871 French P. 777,427, 1935; *Chem. Abs.*, 1935, **29**, 4024.

[142] W. Reppe and W. Wolff, U. S. P. 2,017,355, Oct. 15, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 8001. British P. 430,590, 1935; *Chem. Abs.*, 1935, **29**, 8001.

CONDENSATION OF ACETYLENE WITH HYDROGEN HALIDES

Acetylene and hydrogen halides (in molecular proportions) yield vinyl halides; the latter may react with the halogen halide giving rise to ethylidene dihalides. Perkins[144] made vinyl chloride by passing acetylene at 65°C. into a solution containing 12 per cent hydrochloric acid and 40 per cent catalysts, e.g., equal proportions of cuprous chloride and calcium chloride. Mercuric chloride and anhydrous stannic chloride were used by Toussaint.[145] Baxter[146] employed active carbon, in this instance the catalyst being activated (and reactivated) by a stream of the halide. Reaction temperatures of 100-300°C. and activation temperatures of 200-600°C. were employed. A mixture of vinyl chloride and acetylene is made by the pyrolysis of ethylene dichloride (with inert diluents) at 800-1000°C. Short heating (1-2 sec.) is said to favor the formation of vinyl chloride; diluents, reduced pressure and longer heating (6-8 sec.) promote acetylene formation.[147]

As mentioned previously, vinyl chloride and hydrogen chloride yield ethylidene chloride (*asym.*-dichloroethane). Among the catalysts proposed for this reaction are included the chlorides of aluminum,[148] mercury and zinc.[149] The use of aluminum chloride or ferric chloride in a non-aqueous liquid has also been suggested.[150] According to Kharasch and his associates,[151] hydrogen iodide combines with vinyl chloride to form only ethylidene chloroiodide. Addition of hydrogen bromide to vinyl bromide and to vinyl chloride is influenced by the conditions of the reaction. The presence of peroxides causes the formation of ethylene bromide and bromochloride, respectively. Under peroxide-free conditions the ethylidene compounds are obtained.

Reaction of vinyl chloride with chlorine is said to yield 1,1,2-trichloroethane.[152] Vinyl halides when treated with aqueous solutions of halogens, hypohalogenated acids, hydrogen halides or organic hypohalites form products suggested for refining of mineral oils and purification of gases and also for the manufacture of synthetic resins.[153] Treatment of acetylene with hydrogen fluoride at 0 to 10°C. yields fluorinated compounds which may be employed as insecticides or disinfectants.[154]

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[143] French P. 44,892, 1935, addn. to 724,955, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 6247.

[144] G. A. Perkins, U. S. P. 1,934,324, Nov. 7, 1933, to Carbide and Carbon Chem. Corp.; *Brit. Chem. Abs.* **B**, 1934, 873; *Chem. Abs.*, 1934, **28**, 488. Canadian P. 329,042, 1933; *Chem. Abs.*, 1933, **27**, 1365.

[145] W. J. Toussaint, U. S. P. 1,926,638, Sept. 12, 1933, to Carbide and Carbon Chem. Corp.; *Chem. Abs.*, 1933, **27**, 5756; *Brit. Chem. Abs.* **B**, 1934, 710. Canadian P. 348,472, 1935; *Chem. Abs.*, 1935, **29**, 3353.

[146] J. P. Baxter, U. S. P. 1,944,161, Jan. 23, 1934, to Imperial Chem. Ind. Ltd.; *Chem. Abs.*, 1934, **28**, 2012. British P. 349,017, 1930 (f); *Brit. Chem. Abs.* **B**, 1931, 875; *Chem. Abs.*, 1932, **26**, 1945.

[147] J. P. Baxter, A. M. Edwards and R. M. Winter, British P. 363,009, 1930; *Brit. Chem. Abs.* **B**, 1932, 331; *Chem. Abs.*, 1933, **27**, 1365. German P. 596,256, 1934; *Chem. Abs.*, 1934, **28**, 4436. French P. 721,808, 1931; *Chem. Abs.*, 1932, **26**, 4067.

[148] G. H. Coleman, U. S. P. 1,900,276, March 7, 1933, to Dow Chem. Co.; *Chem. Abs.*, 1933, **27**, 2965.

[149] J. P. Wibaut and J. van Dalfsen, U. S. P. 1,990,968, Feb. 12, 1935, to Dow Chemical Co.; *Chem. Abs.*, 1935, **29**, 2178.

[150] H. S. Nutting, P. S. Petrie and M. E. Huscher, U. S. P. 2,007,144, July 2, 1935, to Dow Chemical Co.; *Chem. Abs.*, 1935, **29**, 5460. See also British P. 454,128, 1936, to Consortium für elektrochem. industrie G.m.b.H.; *Brit. Chem. Abs.* **B**, 1936, 1192. French P. 801,490, 1936; *Chem. Abs.*, 1937, **31**, 420.

[151] M. S. Kharasch, M. C. McNab and F. R. Mayo, *J.A.C.S.*, 1933, **55**, 2521; *Chem. Abs.*, 1933, **27**, 3444; *Brit. Chem. Abs.* **A**, 1933, 805. M. S. Kharasch and C. W. Hannum, *J.A.C.S.*, 1934, **56**, 712; *Chem. Abs.*, 1934, **28**, 2671; *Brit. Chem. Abs.* **A**, 1934, 508.

[152] J. Söll, U. S. P. 1,944,306, Jan. 30, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 2019.

[153] H. P. A. Groll and G. Hearne, British P. 437,573, 1935, to N. V. de Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1936, 138; *Chem. Abs.*, 1936, **30**, 2199. French P. 787,529, 1935; *Chem. Abs.*, 1936, **30**, 1067.

[154] O. Scherer, C. Platz and J. Söll, German P. 621,977, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 2314.

CONDENSATION OF ACETYLENE WITH ORGANIC ACIDS

Analogous to the reaction of acetylene with hydrogen halides is its condensation with organic acids to give vinyl esters and ethylidene diesters. Of the vinyl esters, the acetate is of interest since it can be polymerized alone or co-polymerized with vinyl chloride to form light-colored synthetic resins.[155] In the addition of acetic acid to acetylene, conditions must be carefully regulated if vinyl acetate is the product desired, since the latter tends to react with more acetic acid to form ethylidene diacetate. For liquid-phase production, acetylene is conducted into acetic acid in the presence of a catalyst, the temperature being kept relatively low (not above 60°C.). Excess acetylene, passing through the acid, carries with it most of the vinyl acetate formed together with some acetic acid. One type of catalyst consists of a mercury salt of a disulphonic acid, e.g., methionic, $CH_2(SO_3H)_2$, or benzenedisulphonic acid.[156] Another agent which may be employed is mercuric orthophosphate, prepared by dissolving phosphoric acid and mercuric oxide in the carboxylic acid involved in the reaction.[157] Boron fluoride and hydrofluoric acid have been suggested as promoters for mercury catalysts.[158]

The vapor-phase synthesis of vinyl acetate has been studied by Ushakov and Feinstein.[159] It was pointed out by these workers that liquid-phase reaction is disadvantageous because of the continued presence of excess acetic acid, which favors transformation of vinyl acetate into ethylidene diacetate. With both reactants in the vapor phase it is possible to have an excess of acetylene at all times and thus promote formation of vinyl acetate. The best yields (77-84 per cent) were obtained with 9 parts of acetylene to one of acetic acid led through a reaction tube containing the catalyst. When the latter consisted of zinc or cadmium acetate on activated carbon, a temperature range of 180-250°C. was found most satisfactory.

As previously stated, the ultimate reaction products of acetylene and organic acids are ethylidene diesters. Thus, acetylene passed into warm acetic acid (containing catalysts) gives ethylidene diacetate. For this reaction, Walter[160] proposed a catalyst of silica gel added to a solution of mercuric oxide in sulphuric acid. Rabald[161] suggested a mixture of a mercuric sulphonate and a free disulphonic acid. According to Kuwata and Kato,[162] the efficiency of a catalyst of mercuric sulphate is increased if it is precipitated on Japanese acid clay. This is done by adding fuming sulphuric acid to a mixture of the clay and an acetic acid solution of mercuric acetate. Alkylidene diesters may be formed by passing an acetylene hydrocarbon and an aliphatic acid, both in the vapor phase, through a tube containing pumice and zinc acetate.[163] In the case of ethylidene acetate, the temperature employed was 210-215°C.

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[155] For a detailed description, see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**, Chapter 51.

[156] British P. 427,448, 1935, to C. F. Boehringer & Soehne, G.m.b.H.; *Brit. Chem. Abs.* B, 1935, 619.

[157] F. W. Skirrow and G. O. Morrison, Canadian P. 287,494, 1929, to Canadian Electro Products Co.; *Chem. Abs.*, 1929, **23**, 1908.

[158] W. Weibezahn, U. S. P. 1,912,608, June 6, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, **27**, 4243. British P. 438,728, 1934 (f); *Brit. Chem. Abs.* **B**, 1936, 138; *Chem. Abs.*, 1936, **30**, 2986. German P. 582,544, 1933 and addn. 604,640, 1934; *Chem. Abs.*, 1934, **28**, 778; 1935, **29**, 813. French P. 773,476, 1934; *Chem. Abs.*, 1935, **29**, 1432.

[159] S. N. Ushakov and J. M. Feinstein, *Ind. Eng. Chem.*, 1934, **26**, 561; *Brit. Chem. Abs.* **B**, 1934, 568; *Chem. Abs.*, 1934, **28**, 3711.

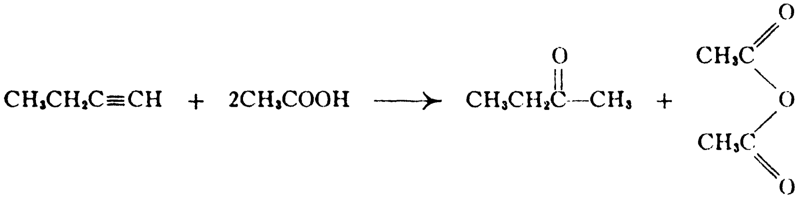
[160] H. Walter, German P. 599,631, 1934, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1934, **28**, 7267; *J. Inst. Pet. Tech.*, 1935, **21**, 28A.

[161] E. Rabald, U. S. P. 2,011,011, Aug. 13, 1935, to C. F. Boehringer & Soehne; *Chem. Abs.*, 1935, **29**, 6609. British P. 427,448, 1935; *Chem. Abs.*, 1935, **29**, 5864; *Brit. Chem. Abs.* **B**, 1935, 619. French P. 770,154, 1934; *Chem. Abs.*, 1935, **29**, 481.

[162] T. Kuwata and O. Kato, *J. Soc. Chem. Ind., Japan*, 1936, **39**, 127; *Brit. Chem. Abs.* **A**, 1936, 807; *Chem. Abs.*, 1936, **30**, 5109.

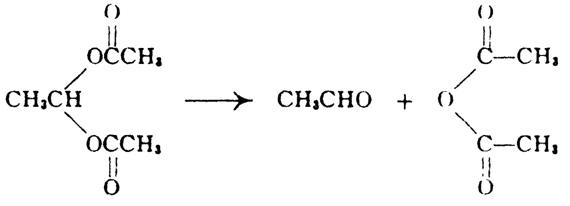
[163] H. Dreyfus, British P. 450,684, 1936; *Chem. Abs.*, 1937, **31**, 110.

By the reaction of acetylene homologues with aliphatic carboxylic acids it is reported that the anhydride of the acid and a ketone corresponding to the acetylene homologue are obtained.[164] Thus, acetic acid and ethylacetylene would react to form acetic anhydride and methyl ethyl ketone.


CH₃CH₂C≡CH + 2CH₃COOH ⟶ CH₃CH₂C(=O)—CH₃ + CH₃C(=O)—O—C(=O)CH₃

Catalysts include salts of mercury, zinc and cadmium mixed with sulphuric or phosphoric acid.

Acetic anhydride and acetaldehyde are produced by the thermal decomposition of ethylidene diacetate[165] according to the reaction:



Müller and Rabald[166] employed silica or alumina gel (treated with aqueous ammonia, hydrochloric acid or active carbon) as carriers with platinum catalysts for the conversion of ethylidene diesters into acid anhydrides. For the same purpose, metals of groups Ib or VIII (except iron, cobalt and nickel) with roughened surfaces have been proposed.[167] Vinyl acetate reacts with liquid hydrogen chloride under atmospheric pressure to give α-chloroethyl acetate in 50-70 per cent yield.[168]

MISCELLANEOUS REACTIONS OF ACETYLENE

The condensation of acetylene with benzene was apparently first studied by Varet and Vienne.[169] They reported that treatment of 200 parts of benzene and 50 parts of aluminum chloride with acetylene yielded a product containing 80 per cent styrene, 15 per cent *asym*-diphenylethane and 5 per cent bibenzyl (*sym*-diphenylethane). Parone[170] stated that ethylbenzene, styrene, bibenzyl and anthracene were produced by this reaction. Cook and Chambers,[171] in attempting to repeat the work of Varet and Vienne, obtained mainly *asym*-diphenylethane and 9-10-dimethylanthracene hydride (10 parts of each from 200 of benzene) with only traces of styrene. Condensation with toluene gave *asym-p.p*-ditolylethane and 2,7-

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[164] O. Nicodemus and W. Weibezahn, German P. 590,237, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 2014.

[165] See also S. N. Kazarnovskii and K. E. Pisarev (*Org. Chem. Ind.* (*U.S.S.R.*), 1936, **1**, 195; *Chem. Abs.*, 1936, **30**, 7543).

[166] R. Müller and E. Rabald, U. S. P. 2,001,211, May 14, 1935, to C. F. Boehringer & Soehne G.m.b.H.; *Chem. Abs.*, 1935, **29**, 4380. German P. 580,930, 1933; *Chem. Abs.*, 1934, **28**, 180. British P. 396,276, 1933; *Brit. Chem. Abs.* B, 1933, 904; *Chem. Abs.*, 1934, **28**, 492. French P. 746,684, 1933; *Chem. Abs.*, 1933, **27**, 4545.

[167] French P. 779,212, 1935, to C. F. Boehringer & Soehne G.m.b.H.; *Chem. Abs.*, 1935, **29**, 4776.

[168] E. Gebauer-Fuelnegg and E. Moffett, *J.A.C.S.*, 1934, **56**, 2009; *Chem. Abs.*, 1934, **28**, 6698; *Brit. Chem. Abs.* A, 1934, 1200.

[169] R. Varet and G. Vienne, *Compt. rend.*, 1886, **104**, 1375; *J.C.S.*, 1887, **52**, 806; *Bull. soc. chim.*, 1887, (2) **47**, 917; *Chem. Zentr.*, 1887, 896.

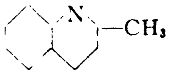
[170] E. Parone, *L'Orosi*, 1902, **25**, 148; *Chem. Zentr.*, 1903, **2**, 662.

[171] O. W. Cook and V. J. Chambers, *J.A.C.S.*, 1921, **43**, 334.

dimethylanthracene (5 parts of each from 200 of toluene) along with small amounts of 2,6-dimethylanthracene and β-methylanthracene. Side reactions yielded xylene, mesitylene and psuedocumene. With the aid of a mercury salt in sulphuric acid, condensation of acetylene with benzene, toluene and ethylbenzene at 10-20°C. has produced ditolylethane (45-50 per cent yield), dixylylethane (50-55 per cent yield) and ethylidene bis-ethylbenzene (20-25 per cent yield) respectively, together with various anthracene derivatives.[172] It has been suggested that petroleum fractions containing aromatic hydrocarbons (e.g., those from Borneo crude) can be refined by treatment with acetylene hydrocarbons at temperatures up to 50°C., in the presence of a diluent (e.g., petroleum ether or cyclohexane) and with the aid of a condensing agent, e.g., boron fluoride or the chlorides of aluminum, iron or zinc.[173] Solid resinous products obtained thereby are said to be applicable in the varnish industry.

Reduction of acetylene by hydrogenation yields first ethylene[174] and then ethane. Reduction to ethylene may also be effected by slightly acid solutions of chromous salts.[175]

Reaction of acetylene with ammonia or amines at elevated temperatures will yield nitriles and pyridine bases. Temperatures of 200-600°C. may be employed and catalysts proposed include non-reducible metal oxides or other compounds such as those of zinc, thorium, vanadium and tungsten or certain free metals, e.g., cadmium, gold, platinum or palladium.[176] This type of synthesis may also be carried out below 200°C. by use of high pressures.[177] Catalytic agents suggested are oxides, hydroxides, alcoholates or anhydrous salts of metals of the first three periodic groups. Thus, ammonia and acetylene heated with zinc chloride at 170-180°C. under 25 atmospheres pressure gave a product believed to be trimethylpyridine. Condensation of acetylene with aniline has been catalyzed in toluene by cuprous or cupric chloride. Kozlov and Fedoseev[178] report that a white solid was produced, which, on distillation, yielded quinaldine,



aniline and a mixture of secondary amines consisting chiefly of tetrahydroquinaldine.

N-Vinyl compounds may be prepared by heating pyrrole (or its derivatives) and acetylene to 100-200°C. under pressure. Alkaline catalysts are suggested. In this manner, N-vinylcarbazole, N-vinylpyrrole and N-vinylindole have been synthesized.[179]

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[172] J. S. Reichert and J. A. Nieuwland, *J.A.C.S.*, 1923, **45**, 3090; *Chem. Abs.*, 1924, **18**, 2000; *J.C.S.*, 1924, **126** (1), 156; *J.S.C.I.*, 1924, **43**, 152B.

[173] British P. 441,806, 1936, to N. V. de Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1936, 260; *Chem. Abs.*, 1936, **30**, 4661. H. I. Waterman, Canadian P. 359,746, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 6937.

[174] See, e.g., W. H. Ross, J. B. Culbertson and J. B. Parsons, *Ind. Eng. Chem.*, 1921, **13**, 775; *J.C.S.*, 1921, **120** (1), 761; *Chem. Abs.*, 1921, **15**, 3610. Also, Carleton Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., Inc., New York, **1930**. K. Sauerwein, U. S. P. 1,860,624, May 31, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, **26**, 3807. German P. 552,008, 1929; *Chem. Abs.*, 1932, **26**, 4347. British P. 325,152 and 325,695, 1929; *Chem. Abs.*, 1930, **24**, 3802, 4051; *Brit. Chem. Abs.* **B**, 1930, 408, 452.

[175] German P. 593,669, 1934, to Compagnie de prod. chim. et electromet. Alais, Froges et Camargue; *Chem. Abs.*, 1934, **28**, 3425. French P. 742,489, 1933; *Chem. Abs.*, 1933, **27**, 3409.

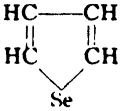
[176] A more detailed discussion is given by Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, **1934**. See also L. Schlecht and H. Rötger, U. S. P. 1,936,995, Nov. 28, 1933; and U. S. P. 2,012,174, Aug. 20, 1935, both to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1052; 1935, **29**, 6608.

[177] British P. 451,794, 1936, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1936, 1083; *Chem. Abs.*, 1937, **31**, 418.

[178] N. S. Kozlov and P. N. Fedoseev, *J. Gen. Chem.* (*U.S.S.R.*), 1936, **6**, 250; *Chem. Abs.*, 1936, **30**, 4864; *Brit. Chem. Abs.* **A**, 1936, 836.

[179] W. Reppe and E. Keyssner, German P. 618,120, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 110. British P. 438,281, 1935; *Brit. Chem. Abs.* **B**, 1936, 140. French P. 790,467, 1935; *Chem. Abs.*, 1936, **30**, 2990.

Acetylene and sulphur at 290-390°C., according to Bhatt and co-workers,[180] gave, in addition to a residue of carbon, a brown liquid containing carbon disulphide, thiophene and thiophenol. Meyer and Sandmeyer[181] obtained carbon, hydrogen sulphide, carbon disulphide and a small amount of thiophene by passing acetylene through molten sulphur.[182] Investigation of the effect of various temperatures was undertaken by Peel and Robinson,[183] the best yield (12 per cent) of thiophene being obtained at 500°C. By an analogous reaction of acetylene and selenium at 400°C., selenophene, is formed, together with naphthalene, anthracene, phenanthrene and stilbene.[184] A liquid believed to be tellurophene (tellurium analogue of thiophene) has been prepared by heating acetylene, aluminum telluride and bauxite to 350-600°C.[185]



Thiophene also results from the reaction of acetylene with hydrogen sulphide. Meyer and Wesche[186] reported that at 640-660°C. small amounts of thionaphthene, C_8H_6S, and thiophthene, $C_6H_4S_2$, were formed in addition to thiophene. Acetylene, hydrogen sulphide and purified coal gas (largely methane) gave α- and β-thiotolene. The use of oxides of aluminum, iron, chromium, nickel, titanium, zinc and thorium as catalysts was studied by Chichibabin.[187] With these contact agents 2 volumes of acetylene and one volume of hydrogen sulphide at 425-450°C. gave thiophene (35 per cent of total yield), ethyl mercaptan, *sec*-butyl mercaptan and α- and β-ethylthiophene. Tomkinson[188] pointed out that sulphides rather than oxides are the catalysts in the above reaction, since in every case the oxide is converted to the sulphide with the formation of water. Using ferric oxide as contact agent one volume of hydrogen sulphide and two volumes of acetylene at 300-350°C. yielded an oily liquid containing acetaldehyde and thiophene (30-40 per cent) and its homologues. The ferric oxide "catalyst" was largely converted to the sulphide during the reaction. Acetylene in contact with iron pyrites at 280-310°C. formed a dark condensate 40 per cent of which was thiophene.[189]

Liquid hydrogen sulphide and gaseous acetylene give a small percentage of thioacetaldehyde, according to Guest.[190] Reaction of hydrogen sulphide in aqueous solution with acetylene under 10-20 atmospheres pressure and at 100°C. is said to form α-trithioaldehyde. Ethyl mercaptan and vinylethyl sulphide result if equal volumes of hydrogen sulphide and acetylene are passed through diethylene glycol containing a small percentage of potassium hydrosulphide.[191] With an excess of acetylene the main product is the diethyl ether of ethanedithiol.

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[180] C. T. Bhatt, K. S. Nargund, D. B. Kanga and M. S. Shah, *J. Univ. Bombay*, 1934, **3**, 159; *Chem. Abs.*, 1935, **29**, 4762; *Brit. Chem. Abs.* **A**, 1935, 325.

[181] V. Meyer and T. Sandmeyer, *Ber.*, 1883, **16**, 2176; *J.C.S.*, 1884, **46**, 45.

[182] G. Capelle (*Bull. soc. chim.*, 1908, (4) **3**, 150; *Chem. Abs.*, 1908, **2**, 1562; *J.C.S.*, 1908, **94** (1), 201) reported that the principal product of this reaction is thiophthene, $C_6H_4S_2$. This was confirmed by W. O. de Coninck, *Bull. acad. roy. Belgique*, **1908**, 303; *Chem. Abs.*, 1909, **3**, 643; *J.C.S.*, 1908, **94** (1), 750.

[183] J. B. Peel and P. L. Robinson, *J.C.S.*, **1928**, 2068; *Brit. Chem. Abs.* **A**, 1928, 1112; *Chem. Abs.*, 1928, **22**, 4460.

[184] H. V. A. Briscoe and J. B. Peel, *J.C.S.*, **1928**, 1741; *Chem. Abs.*, 1928, **22**, 3657; *Brit. Chem. Abs.* **A**, 1928, 1021.

[185] F. A. McMahon, T. G. Pearson and P. L. Robinson, *J.C.S.*, **1933**, 1644.

[186] R. Meyer and H. Wesche, *Ber.*, 1917, **50**, 422; *J.C.S.*, 1917, **112** (1), 313.

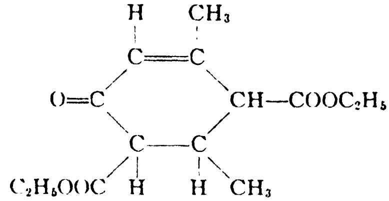
[187] A. E. Chichibabin, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 703; *Chem. Abs.*, 1915, **9**, 2512. A. E. Chichibabin and O. S. Bagdassarjanz, *J. prakt. Chem.*, 1924, **108**, 200; *Chem. Abs.*, 1925, **19**, 34.

[188] M. G. Tomkinson, *J.C.S.*, 1924, **125**, 2264; *Chem. Abs.*, 1925, **19**, 463; *J.C.S.*, 1925, **128** (1): 58.

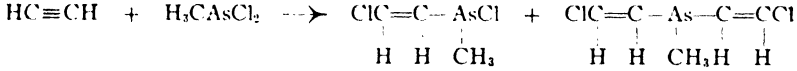
[189] W. Steinkopf and G. Kirchhoff, *Ann.*, 1914, **403**, 1; *Chem. Abs.*, 1914, **8**, 1416; *J.C.S.*, 1914, **106** (1), 425. W. Steinkopf and J. Herold, *Ann.*, 1922, **428**, 123; *Chem. Abs.*, 1922, **16**, 3653; *J.C.S.*, 1922, **122** (1), 850.

[190] H. P. Guest, *Iowa State Coll. J. Sci.*, 1933, **8**, 197; *Chem. Abs.*, 1934, **28**, 2631.

Gustafson[192] pointed out that acetylene reacts at 70-80°C. with ethylacetoacetate in the presence of mercuric sulphate and sulphuric acid. The products obtained were identified as ethyl 3,5-dimethyl-2-cyclohexene-1-one-4-carboxylate (b.p., 102-104°C. at 0.12 mm.) and diethyl 3,5-dimethyl-2-cyclohexene-1-one-4,6-dicarboxylate (b.p., 128-130°C. at 0.12 mm.). The latter compound is represented below:



According to Das-Gupta,[193] acetylene reacts with dichloromethylarsine, CH_3-$AsCl_2$, in the presence of anhydrous aluminum chloride at 10-15°C. The products, β-chlorovinylmethylchloroarsine (b.p. 112-115°C. at 10 mm.) and β,β-dichlorovinylmethylarsine (b.p., 140-145°C. at 10 mm.) are shown in the following equation representing the reaction:



$$HC\equiv CH + H_3CAsCl_2 \longrightarrow \underset{H}{ClC}=\underset{H}{C}-\underset{CH_3}{As}Cl + \underset{H}{ClC}=\underset{H}{C}-\underset{CH_3}{As}-\underset{H}{C}=\underset{H}{C}Cl$$

The second product was also obtained by further reacting the first product with acetylene at 5 to 10°C., using the aluminum chloride catalyst.

Dimethylethinylcarbinol, $CH\equiv CC(CH_3)_2OH$, is produced when acetone (1 mol), potassium hydroxide (1 mol) and calcium carbide (1 mol) are suspended in ether for 24 hours at 0°C., with subsequent addition of water.[194] Oxidation of this carbinol by passing it over anhydrous magnesium sulphate at elevated temperature yields isopropenylacetylene, according to Favorskii.[195] Reaction of isopropenvlacetylene with hydrochloric acid, using cuprous chloride as catalyst, gives chloroisoprene.[196] By catalytic addition of hydrochloric acid to dimethylethinylcarbinol, dimethylchlorovinylcarbinol is formed.[197] Methyl β-chlorovinyl ketone results from reaction of acetylene with acetyl chloride at 15°C., using aluminum chloride as catalyst.[198] Schroeter[199] reports that crystalline acetaldehydedisulphonic acid is prepared by saturating fuming sulphuric acid with acetylene and allowing to stand for several weeks in the absence of moisture.

REACTIONS OF ACETYLENE HOMOLOGUES

Because of their relative difficulty of preparation, the homologues of acetylene have received only slight attention as compared with acetylene itself. One method of preparation is by the reaction of organic halides with sodium acetylide.[200] The latter is made by passing acetylene into a solution of metallic sodium in liquid ammonia until the blue color has disappeared. In this manner, methyl iodide and sodium acetylide yield methylacetylene (allylene). Likewise, methylacetylene added to sodium in liquid ammonia gives sodium methylacetylide, which in turn reacts with methyl iodide to form dimethylacetylene:

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[191] French P. 793,151, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 4240.

[192] C. Gustafson, *Finska Kemistsamfundets Medd.*, 1935, **44**, 85; *Chem. Abs.*, 1936, **30**, 5561. See also B. Ciocca and M. Scattola, *Gazz. chim. ital.*, 1936, **66**, 394; *Brit. Chem. Abs.* **A**, 1936, 1249.

[193] H. N. Das-Gupta, *J. Indian Chem. Soc.*, 1936, **13**, 305; *Chem. Abs.*, 1936, **30**, 7098; *Brit. Chem. Abs.* **A**, 1936, 1097.

[194] L. Kazarian, *J. Gen. Chem.* (*U.S.S.R.*), 1934, **4**, 1347; *Brit. Chem. Abs.* **A**, 1935, 729; *Chem. Abs.*, 1935, **29**, 3978.

[195] A. E. Favorskii, Russian P. 31,015, 1933; *Chem. Abs.*, 1934, **28**, 3425.

[196] A. E. Favorskii, Russian P. 31,016, 1933; *Chem. Abs.*, 1934, **28**, 3425.

[197] A. E. Favorskii, Russian P. 34,544, 1934; *Chem. Abs.*, 1935, **29**, 2976.

[198] A. Cornillot and R. Alquier, *Compt. rend.*, 1935, **201**, 837; *Chem. Abs.*, 1936, **30**, 1735.

[199] G. Schroeter, German P. 632,610, 1936; *Chem. Abs.*, 1937, **31**, 117.

$$2CH_3C{\equiv}CH + 2Na \longrightarrow 2CH_3C{\equiv}CNa + CH_3CH{=}CH_2$$
$$CH_3C{\equiv}CNa + CH_3I \longrightarrow CH_3C{\equiv}CCH_3 + NaI$$

Calcium acetylide may be obtained either by passing acetylene into a solution of metallic calcium in liquid ammonia or by adding the latter solution to one of acetylene in liquid ammonia. The second method is the more rapid, according to Vaughn and Danehy.[201] These workers obtained pure 1-butyne in theoretical yield from diethyl sulphate and calcium acetylide in liquid ammonia. Amyl chloride, amyl bromide and butyl bromide likewise react with calcium acetylide to give amylacetylene and butylacetylene, respectively.

Another method of preparing alkylacetylenes is by dehydrohalogenation of certain organic halides by sodium[202] or sodamide[203] in liquid ammonia. With sodium, phenylacetylene was obtained in 96 per cent yield from β-bromostyrene and in 66 per cent yield from styrene dibromide. Also, by the same method p-methyl-α-chlorostyrene gave a 63 per cent yield of tolylacetylene. By employing sodamide, phenylacetylene may be procured from α-chlorostyrene, β-bromostyrene and styrene dibromide, butylacetylene from butyliodoacetylene, amylacetylene from 1,2-dibromoheptene, hexylacetylene from 2-bromo-1-octene and octylacetylene from 1,2-dibromodecane. The sodamide was prepared from sodium in liquid ammonia, using ferric nitrate as catalyst. Bachman and Hill[204] made 1-heptyne by dehalogenation of various bromo and chloro derivatives of heptane and heptene. Vapor-phase dehalogenation was effected with soda lime; liquid-phase with potassium hydroxide suspended in mineral oil. In Table 152 the boiling points of a number of allene and acetylene hydrocarbons are given.[205]

Although acetylene polymerizes to mono- and divinylacetylene in an acid solution of cuprous and ammonium salts,[206] some of the monosubstituted acetylenes do not act in an analogous way.[207] For instance, when phenylacetylene is heated in an acid solution of cuprous chloride and ammonium chloride, a yellow complex, $C_{16}H_{10}{\cdot}CuCl$, is formed, which is readily decomposed by ether to diphenylbiacetylene, $C_6H_5C{\equiv}CC{\equiv}CC_6H_5$.

The condensation of alkylacetylenes wtih methanol, employing a mercuric oxide-boron trifluoride catalyst,[208] yields ketals (2,2-dimethoxyalkanes). With acetic acid in place of methanol, α-alkylvinyl esters result.[209] In acid solution ketals are

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[200] See P. Lebeau and M. Picon, *Compt. rend.*, 1913, **156**, 1077; *Chem. Abs.*, 1913, **7**, 2386. T. Y. Lai, *Bull. soc. chim.*, 1933, (4) **53**, 687; *Brit. Chem. Abs.* **A**, 1933, 1270. O. Maass and J. Russell, *J.A.C.S.*, 1921, **43**, 1227. F. R. Morehouse and O. Maass, *Can. J. Research*, 1931, **5**, 306; 1934, **11**, 637; *Chem. Abs.*, 1932, **26**, 354; 1935, **29**, 1059.

[201] T. H. Vaughn and J. P. Danehy, *Proc. Indiana Acad. Sci.*, 1934, **44**, 144; *Chem. Abs.*, 1936, **30**, 428.

[202] T. H. Vaughn, *J.A.C.S.*, 1934, **56**, 2064; *Chem. Abs.*, 1935, **29**, 115; *Brit. Chem. Abs.* **A**, 1934, 1330; *J. Inst. Pet. Tech.*, 1934, **20**, 609A.

[203] T. H. Vaughn, R. R. Vogt and J. A. Nieuwand, *J.A.C.S.*, 1934, **56**, 2120; *Chem. Abs.*, 1935, **29**, 115; *Brit. Chem. Abs.* **A**, 1934, 1330.

[204] G. B. Bachman and A. J. Hill, *J.A.C.S.*, 1934, **56**, 2730; *Brit. Chem. Abs.* **A**, 1935, 193; *Chem. Abs.*, 1935, **29**, 724; *J. Inst. Pet. Tech.*, 1935, **21**, 47A. A. J. Hill and F. Tyson, *J.A.C.S.*, 1928, **50**, 172; *Chem. Abs.*, 1928, **22**, 380; *Brit. Chem. Abs.* **A**, 1928, 269.

[205] O. Nicodemus, *Angew. Chem.*, 1936, **49**, 787; *Chem. Abs.*, 1937, **31**, 477.

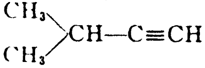
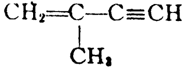
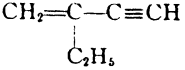
[206] *Cf.* discussion of this in forepart of this chapter.

[207] Y. S. Zalkind and F. B. Funduiler, *Ber.*, 1936, **69**, 128; *Chem. Abs.*, 1936, **30**, 2932.

[208] A proposed mechanism for mercury catalysis in acetylene addition has been made by G. F. Hennion, R. R. Vogt and J. A. Nieuwland (*J. Org. Chem.*, 1936, **1**, 159; *Chem. Abs.*, 1936, **30**, 7097).

[209] G. F. Hennion, D. B. Killian, T. H. Vaughn and J. A. Nieuwland, *J.A.C.S.*, 1934, **56**, 1130; *Chem. Abs.*, 1934, **28**, 4374; *Brit. Chem. Abs.* **A**, 1935, 193. D. B. Killian, G. F. Hennion and J. A. Nieuwland, *J.A.C.S.*, 1934, **56**, 1384; *Chem. Abs.*, 1934, **28**, 4374; *Brit. Chem. Abs.* **A**, 1934, 867. G. F. Hennion and J. A. Nieuwland, *J.A.C.S.*, 1935, **57**, 2006; *Chem. Abs.*, 1935, **29**, 7939;

TABLE 152.—*Allene and Acetylene Hydrocarbons.*

Empirical Formula	Name	Constitution	Boiling Point °C.
C_2H_2	Acetylene	$CH\equiv CH$	−83
C_4H_6	Methylallene	$CH_3CH=C=CH_2$	18
	Ethylacetylene	$CH_3—CH_2—C\equiv CH$	8.5
	Dimethylacetylene	$CH_3—C\equiv C—CH_3$	27-28
C_5H_8	*n*-Propylacetylene	$CH_3—CH_2—CH_2—C\equiv CH$	40
	Methylethylacetylene	$CH_3—CH_2—C\equiv C—CH_3$	55
	Isopropylacetylene	 $(CH_3)_2CH—C\equiv CH$	28
	Dimethylallene	$CH_3—CH=C=CH—CH_3$	41
C_4H_2	Diacetylene	$CH\equiv C—C\equiv CH$	9.5
C_4H_4	Vinylacetylene	$CH_2=CH—C\equiv CH$	5
C_5H_6	α-Methyl-β-vinylacetylene	$CH_2=CH—C\equiv C—CH_3$	59
	2-Methyl-vinylacetylene	 $CH_2=C(CH_3)—C\equiv CH$	33
C_6H_8	α-Ethyl-β-vinylacetylene	$CH_2=CH—C\equiv C—C_2H_5$	85
	2-Ethyl-vinylacetylene	 $CH_2=C(C_2H_5)—C\equiv CH$	66
C_6H_6	Dipropargyl	$CH\equiv C—CH_2—CH_2—C\equiv CH$	86
	Methylpropargylacetylene	$CH_3—C\equiv C—CH_2—C\equiv CH$	78-83
	Butadienylacetylene	$CH_2=CH—CH=CH—C\equiv CH$	84
	Divinylacetylene	$CH_2=CH—C\equiv C—CH=CH_2$	83-84
	Dimethyldiacetylene	$CH_2—C\equiv C—C\equiv C—CH_3$	129-130
C_8H_8	Vinylbutadienylacetylene	$CH_2=CH—C\equiv C—CH=CH—CH=CH_2$	43-45 (11 mm.)
C_8H_6	Divinyldiacetylene	$CH_2=CH—C\equiv C—C\equiv C—CH=CH_2$	33 (9 mm.)

quite unstable, hydrolyzing to methanol and the corresponding ketone. The mechanism of ketal formation is thought to be stepwise, the intermediate products being vinyl ethers. Reaction of monohydric alcohols (other than methanol) with alkylacetylenes, employing the above-mentioned catalyst, yielded polymeric products only, from which no ketals could be isolated. It was then found that with the addition of a small percentage of trichloroacetic acid to the catalyst, high yields of 2,2-dialkoxyalkanes were obtained from straight-chain monohydric alcohols and alkylacetylenes.[210] It is reported that under peroxide-free conditions methylacetylene adds hydrogen bromide to form 2,2-di-bromopropane, but in the presence of peroxides 1,2-bibromopropane results.[211] Similar experiments were conducted with butylacetylene.[212] In the absence of peroxides, the products were 2-bromo-1-hexene and 2,2-dibromohexane, but 1-bromo-1-hexene and 1,2-dibromohexane were found with peroxides present.[213]

Alkylacetylenes have been found to condense with polyhydric alcohols and

Brit. Chem. Abs. **A**, 1935, 1480. D. B. Killian, G. F. Hennion and J. A. Nieuwland, *J.A.C.S.*, 1936, **58**, 892; *Chem. Abs.*, 1936, **30**, 5174; *Brit. Chem. Abs.* **A**, 1936, 961.

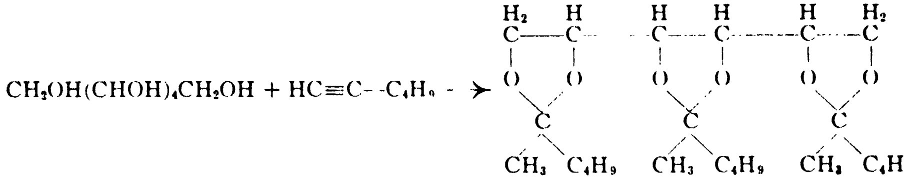
[210] D. B. Killian, G. F. Hennion and J. A. Nieuwland, *J.A.C.S.*, 1936, **58**, 80.

[211] M. S. Kharasch, J. G. McNab and M. C. McNab, *J.A.C.S.*, 1935, **57**, 2463; *Brit. Chem. Abs.* **A**, 1936, 310; *Chem. Abs.*, 1936, **30**, 1734; *J. Inst. Pet. Tech.*, 1936, **22**, 87A.

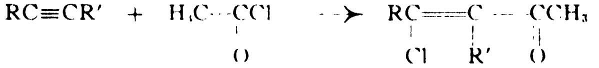
[212] C. A. Young, R. R. Vogt and J. A. Nieuwland, *J.A.C.S.*, 1936, **58**, 1806; *Chem. Abs.*, 1936, **30**, 7542; *Brit. Chem. Abs.* **A**, 1936, 1359.

[213] For a discussion of the peroxide effect on addition of hydrogen bromide to acids having triple bonds, see P. L. Harris and J. C. Smith, *J.C.S.*, 1935, 1572; *Brit. Chem. Abs.* **A**, 1936, 53; *Chem. Abs.*, 1935, **29**, 7278.

α-hydroxy acids to form dioxolanes and dioxolones.[214] For example, with catalysts of mercuric oxide and boron trifluoride in methanol, mannitol and butylacetylene yielded 2-butyl-2-methyl-4,5-bis-(2-butyl-2-methyl-1,3-dioxolan-4-yl)-dioxolane (b.p., 210-212°C. at 9 mm.). This reaction is represented as follows:



The investigation of the reaction between acetyl chloride and alkylacetylenes has been carried out by Kroeger, Sowa and Nieuwland.[215] The main reaction involving the formation of chloro-olefinic ketones is represented as follows:



$$RC{\equiv}CR' + H_3C-\underset{O}{\overset{\|}{C}}Cl \longrightarrow R\underset{Cl}{C}=\underset{R'}{C}-\underset{O}{C}CH_3$$

These workers found stannic chloride, in 2 to 4 per cent concentrations, to be the most effective catalyst. The experiments of Ryden and Marvel[216] show that sulphur dioxide reacts with monosubstituted acetylenes to form polysulphones, whereas the disubstituted derivatives do not add in this manner.

Primary acetylenic alcohols of the type $RC{\equiv}CCH_2OH$ may be prepared by the action of formaldehyde vapor on the Grignard derivatives of the corresponding alkylacetylenes.[217] Reaction of acetylene with alkyl mercury bromides yields the corresponding bis-(alkylmercury) acetylides.[218]

Grignard reagents enter several other reactions involving acetylenes.[219] For example, allyl bromide reacts with *n*-butylacetylenemagnesium bromide in the presence of anhydrous cuprous chloride to yield *n*-butylallylacetylene (b.p., 58°C. at 22 mm.). This may be represented as follows:

$$C_4H_9-C{\equiv}C-MgBr + H_2C{=}CH-CH_2Br \longrightarrow C_4H_9-C{\equiv}C-CH_2-CH{=}CH_2$$

The addition of alkyl sulphates to acetylenic Grignard reagents has been described by Thorn, Hennion and Nieuwland.[220] Using metal halides, Danehy and Nieuwland[221] prepared diacetylenes, such as diphenyldiacetylene from cupric bromide and phenylacetylene magnesium bromide.

The isolation of the hydrogen isotope, deuterium,[222] and the possibility of obtaining significant quantities of heavy water (deuteriowater) as a source of deuterium[223] have led to some investigation of the synthesis and properties of deuterioacetylene. One method of preparation is by the action of heavy water on calcium carbide. Clemo and McQuillen[224] state that the action of 99 per cent heavy water on calcium carbide results in a 60 per cent yield of deuterioacetylene. The latter compound is made also by isotopic exchange between acetylene and heavy water.[225]

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[214] D. B. Killian, G. F. Hennion and J. A. Nieuwland, *J.A.C.S.*, 1936, **58**, 1658; *Chem. Abs.*, 1936, **30**, 7541.

[215] J. W. Kroeger, F. J. Sowa and J. A. Nieuwland, *J. Org. Chem.*, 1936, **1**, 163; *Chem. Abs.*, 1936, **30**, 7097.

[216] L. L. Ryden and C. S. Marvel, *J.A.C.S.*, 1936, **58**, 2047; *Chem. Abs.*, 1936, **30**, 8184; *Brit. Chem. Abs.* **A**, 1936, 1486.

[217] H. H. Guest, *J.A.C.S.*, 1925, **47**, 860; *Chem. Abs.*, 1925, **19**, 1244; *J.C.S.*, 1925, **128** (1), 627.

[218] R. J. Spahr, R. R. Vogt and J. A. Nieuwland, *J.A.C.S.*, 1933, **55**, 2465; *Brit. Chem. Abs.* **A**, 1933, 815; *Chem. Abs.*, 1933, **27**, 3445. T. H. Vaughn, R. J. Spahr and J. A. Nieuwland, *J.A.C.S.*, 1933, **55**, 4206; *Chem. Abs.*, 1933, **27**, 5718; *Brit. Chem. Abs.* **A**, 1933, 1282.

[219] J. P. Danehy, D. B. Killian and J. A. Nieuwland, *J.A.C.S.*, 1936, **58**, 611; *Chem. Abs.*, 1936, **30**, 3772.

[220] S. D. Thorn, G. F. Hennion and J. A. Nieuwland, *J.A.C.S.*, 1936, **58**, 796; *Brit. Chem. Abs.* **A**, 1936, 819; *Chem. Abs.*, 1936, **30**, 4807; *J. Inst. Pet. Tech.*, 1936, **22**, 298A.

[221] J. P. Danehy and J. A. Nieuwland, *J.A.C.S.*, 1936, **58**, 1609; *J. Inst. Pet. Tech.*, 1936, **22**, 538A.

[222] H. C. Urey, *Ind. Eng. Chem.*, 1934, **26**, 803; *Chem. Abs.*, 1934, **28**, 4977.

[223] E. W. Washburn and H. C. Urey, *Proc. Nat. Acad. Sci.*, 1932, **18**, 496; *Chem. Abs.*, 1932, **26**, 5003. H. C. Urey, *Science*, 1933, **78**, 566; *Chem. Abs.*, 1934, **28**, 1922; *Brit. Chem. Abs.* **A**,

$$C_2H_2 + D_2O \rightleftharpoons C_2D_2 + H_2O$$

It has been noted that deuterioacetylene, under the influence of x-rays, undergoes polymerization at about the same rate as ordinary acetylene.[226] Clemo and McQuillen[227] reported that deuterioacetylene under controlled conditions may be polymerized to hexadeuteriobenzene. Deuterioacetaldehyde has been prepared by the hydration of deuterioacetylene in an acid solution of mercury salts in heavy water.[228]

1934, 156. G. N. Lewis, *J.A.C.S.*, 1933, **55**, 1297; *Brit. Chem. Abs.* **A**, 1933, 442; *Chem. Abs.*, 1933, **27**, 2092. G. N. Lewis and R. E. Cornish, *J.A.C.S.*, 1933, **55**, 2616; *Chem. Abs.*, 1933, **27**, 3394; *Brit. Chem. Abs.* **A**, 1933, 793. G. N. Lewis and R. T. MacDonald, *J.A.C.S.*, 1933, **55**, 3057; *J. Chem. Phys.*, 1933, **1**, 341; *Chem. Abs.*, 1933, **27**, 3664, 4147; *Brit. Chem. Abs.* **A**, 1933, 894.

[224] G. R. Clemo and A. McQuillen, *J.C.S.*, **1935**, 851; *Chem. Abs.*, 1935, **29**, 5820; *Brit. Chem. Abs* **A**, 1935, 967. See also A. Klemenc and O. B. von Frugnoni, *Naturwissenschaften*, 1934, **22**, 465; *Chem. Abs.*, 1934, **28**, 7243; *Brit. Chem. Abs.* **A**, 1934, 990.

[225] L. H. Reyerson and S. T. Yuster, *J.A.C.S.*, 1934, **56**, 1426; *Chem. Abs.*, 1934, **28**, 4373; *Brit. Chem. Abs.* **A**, 1934, 853. R. P. Bell, *J.A.C.S.*, 1935, **57**, 778; *Chem. Abs.*, 1935, **29**, 3596; *Brit. Chem. Abs.* **A**, 1935, 713. Equilibrium studies of this reaction and others involving deuterium compounds of water and acetylene have been contributed by L. H. Reyerson (*J.A.C.S.*, 1935, **57**, 779; *Brit. Chem. Abs.* **A**, 1935, 713; *Chem. Abs.*, 1935, **29**, 3596), L. H. Reyerson and B. Gillespie (*J.A.C.S.*, 1935, **57**, 2250; 1936, **58**, 282; *Chem. Abs.*, 1936, **30**, 1288, 2469; *Brit. Chem. Abs.* **A**, 1936, 29, 427) and K. Hirota and G. Okamoto (*Bull. Chem. Soc. Japan*, 1936, **11**, 349; *Chem. Abs.*, 1936, **30**, 6269).

[226] S. C. Lind, J. C. Jungers and C. H. Schiflett, *J.A.C.S.*, 1935, **57**, 1032; *Chem. Abs.*, 1935, **29**, 5350; *Brit. Chem. Abs.* **A**, 1935, 943. *Cf.* polymerization of acetylene by light rays, in first portion of this chapter

[227] G. R. Clemo and A. McQuillen, *loc. cit.*

[228] J. E. Zanetti and D. V. Sickman, *J.A.C.S.*, 1935, **57**, 2735; *Chem. Abs.*, 1936, **30**, 1737; *Brit. Chem. Abs.* **A**, 1936, 316.

Chapter 29

Halogenation of Methane. Properties and Uses of Halogen Derivatives

Methods of chlorination of methane may be conveniently subdivided into three main divisions, viz.: thermal, catalytic and photochemical.[1] In all of these methods it is essential that temperature control be rigorously maintained, otherwise reaction between methane and chlorine may proceed with formation of carbon and hydrogen chloride, often with explosive violence. In purely thermal operations temperatures of 250-300°C. are generally employed, though with short times of contact as high as 1400°C. has been recommended. Inert diluents, such as nitrogen, are helpful in controlling the rate of reaction. Many types of catalysts have been suggested, as for example, antimony pentachloride, ferrous or ferric chloride, partially reduced cupric chloride, activated carbon and pumice. Combination of methane and chlorine is accelerated also by light radiation, such as sunlight, actinic rays, light from a carbon arc, metallic filament, or mercury vapor lamp. The advantage of photochemical chlorination appears to be that it can be effected at room temperature or lower. However, in most instances careful control of illumination is necessary to prevent the reaction from getting out of hand.

In all cases the products consist of a mixture of chlorinated hydrocarbons, though by selecting proper conditions a preponderance of one chloro-methane may be obtained. Thus, Giordani[2] reports that methane and chlorine, in the ratio of 9:1, conducted over a catalyst at 450°C. furnished an 89 per cent yield of methyl chloride. The contact agent was partially reduced cupric chloride containing 1 per cent of cerium chloride. Dilution of the reactants with hydrogen chloride and use of higher temperatures yields mainly carbon tetrachloride. In this manner Kiprianov and Kusner[3] secured a 90 per cent yield of the tetrachloride by passage of methane, chlorine and hydrogen chloride (16:64:[80-100] liters) over activated carbon at 525-530°C. Tomasik[4] recommends employing air in place of chlorine. For example, 70 per cent of the chlorine in a gaseous mixture of methane, hydrogen chloride and air (2:9:18) was converted, at 400°C. in the presence of cupric chloride, into chlorinated products. Of the latter 90 per cent was carbon tetrachloride.

PROPERTIES AND USES OF CHLOROETHANES

Methyl chloride, CH_3Cl, is a colorless gas possessing a characteristic odor and burning with a white flame. It can be condensed to a liquid boiling at —24°C.

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[1] For reviews of these methods, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934. See also, T. S. Wheeler, *J. Indian Chem. Soc.*, Prafulla Chandra Ray Commemoration Vol., **1933**, 53; *Chem. Abs.*, 1934, **28**, 93; *Brit. Chem. Abs.* **B**, 1933, 539. J. H. Frydlender, *Rev. prod. chim.*, 1934, **37**, 707, 737; *Chem. Abs.*, 1935, **29**, 7935. F. C. Whitmore, "Organic Chemistry," D. Van Nostrand Co., Inc., New York, **1937**. J. v. Braun, *Bull. soc. chim.*, 1936, **3**, 1919.

[2] M. Giordani, *Ann. chim. applicata*, 1935, **25**, 163; *Chem. Abs.*, 1935, **29**, 6206; *Brit. Chem. Abs.* **B**, 1935, 617. *IX Congr. intern. quim. pura applicada*, 1934, **4**, 371; *Chem. Abs.*, 1936, **30**, 3914.

[3] A. I. Kiprianov and T. S. Kusner, *J. Applied Chem.* (*U.S.S.R.*), 1935, **8**, 673; *J. Inst. Pet. Tech.*, 1936, **22**, 142A; *Chem. Abs.*, 1936, **30**, 1735; *Brit. Chem. Abs.* **B**, 1935, 938.

[4] Z. Tomasik, *Przemysl Chem.*, 1934, **18**, 598; *J. Inst. Pet. Tech.*, 1935, **21**, 202A; *Brit. Chem. Abs.* **B**, 1935, 137; *Chem. Abs.*, 1935, **29**, 6206.

at 760 mm. Its critical temperature and pressure are 143.1°C. and 65.8 atmospheres, respectively. This chloromethane may be employed as a refrigerant, particularly when dissolved in a solvent such as a mixture of α- and β-chloronaphthalenes[5] or β,β'-dichloroethyl ether,[6] and (under pressure) as a diluent in the dewaxing of mineral oils.[7] Stabilization, or prevention of development of acidity, of liquid methyl chloride is accomplished by incorporation of a small proportion (0.001 to 1 per cent) of phenolic substances, such as phenol, resorcinol, *p*-cresol, or α-naphthol.[8]

Hydrolysis of this chloride with steam at 400°C. furnished 16 per cent methyl alcohol and a like percentage of formaldehyde.[9] The ratio of chloride to steam should be 1:10 and the yields can be increased by recycling the residual gases. Tin phosphate on pumice was a satisfactory catalyst, but titanium dioxide or a mixture of tin and iron phosphates proved unsatisfactory. Also, it has been reported that methyl chloride may be condensed with aldehydes to produce saturated hydrocarbons.[10] Thus, the above halide was heated with formaldehyde to 350°C. A small proportion of cupric oxide was incorporated in the reaction zone to aid in the condensation. The interaction of methyl chloride and carbon monoxide has been utilized in the production of acetyl chloride.[10a] In the procedure, the two reactants, at a temperature of 860°C., are led over a copper catalyst for a period of 0.3 second.

By progressive chlorination of chloromethane there are obtained methylene chloride, chloroform and carbon tetrachloride.[11] Mixed with one-third its volume of chlorine and heated to 360-380°C., methyl chloride gives principally methylene chloride.[12] On the other hand when a larger proportion (46 per cent by volume) of chlorine and temperatures of 400° to 650°C. are employed, followed by further addition of the halogen (85 per cent by volume of the halides present) and reheating, both methylene chloride and chloroform are secured.[13] Levine[14] recommends using a mixture of methyl chloride, ethylene chloride and chlorine (in the volume-ratio of 2:2:1 to 4:3:1) and temperatures of 400° to 500°C. When chlorination is complete the gases are cooled to 200°C., 1 to 1.5 volumes of chlorine added and the reactants again subjected to the higher temperatures. This procedure results in a 15 to 30 per cent yield of chloroform.

[5] G. F. Zellhoefer, U. S. P. 1,991,188, Feb. 12, 1935; *Chem. Abs.*, 1935, **29**, 2034. A comparison of the dehydrators which may be used in refrigerating lines employing monochloromethane is given by G. H. Clark, *Refrigerating Eng.*, 1936, **31**, 366; *Chem. Abs.*, 1936, **30**, 5467. *Cf.* H. D. Edwards, *Refrigerating Eng.*, 1936, **31**, 356; *Chem. Abs.*, 1936, **30**, 5681.

[6] G. F. Zellhoefer, U. S. P. 1,991,240, Feb. 12, 1935; *Chem. Abs.*, 1935, **29**, 2034; *Brit. Chem. Abs.* **B**, 1935, 1074. For a discussion of the toxicity of methyl chloride, see A. Weinstein, *J. Am. Med. Assoc.*, 1937, **108**, 1603. A. H. Kegel, W. D. McNally and A. S. Pope, *J. Am. Med. Assoc.*, 1929, **93**, 353; *Chem. Abs.*, 1930, **24**, 4561. Report of the Committee on Poisonous Gases of the American Medical Association, *J. Am. Med. Assoc.*, 1930, **94**, 1832. H. B. Porteous, *Brit. Med. J.*, **1930** (1), 414. B. B. Sharp, *Brit. Med. J.*, **1930** (1), 336. A. P. Gorham, *Brit. Med. J.*, **1934** (1), 529. A. Van der Kloot, *Illinois Med. J.*, 1934, **65**, 508. C. A. Birch, *Lancet*, **1935** (1), 259; *Chem. Abs.*, 1935, **29**, 2233; *Brit. Chem. Abs.* **A**, 1935, 525. O. Roth, *Schweiz. Z. Unfällk.* 1923, 17, 169.

[7] H. Ramser, U. S. P. 2,009,454, July 30, 1935, to Edeleanu G.m.b.H.; *Chem. Abs.*, 1935, **29**, 6418; *J. Inst. Pet. Tech.*, 1935, **21**, 383A. The properties of halogenated hydrocarbon solvents are reviewed by P. J. Wiezevich and H. G. Vesterdal, *Chem. Rev.*, 1936, **19**, 101; *Chem. Abs.*, 1937, **31**, 175; *J. Inst. Pet. Tech.*, 1937, **23**, 32A.

[8] P. J. Carlisle and C. R. Harris, Canadian P. 341,792, 1934, to Canadian Industries, Ltd.; *Chem. Abs.*, 1934, **28**, 5076. For the toxicity of methyl chloride and other chlorine derivatives of methane, see K. B. Lehman and L. Schmidt-Kehl, *Arch. Hyg. Bakt.*, 1936, **116**, 131; *Chem. Abs.*, 1937, **31**, 477.

[9] A. Abkin and S. Medvedev, *J. Ind. Chem.* (*Moscow*), **1934**, No. 1, 34; *Chem. Abs.*, 1934, **28**, 3050; *Brit. Chem. Abs.* **B**, 1934, 616.

[10] German P. 629,897, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 6006.

[10a] P. J. Wiezevich and P. K. Frolich, U. S. P. 2,062,344, Dec. 1, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1937, **31**, 708.

[11] Descriptions of such procedures are given by Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[12] W. Berndt and O. Ernst, U. S. P. 1,964,868, July 3, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5080.

[13] P. J. Carlisle, U. S. P. 1,939,292, Dec. 12, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1934, 872.

[14] A. A. Levine, U. S. P. 1,975,727, Oct. 2, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 839; *Chem. Abs.*, 1934, **28**, 7268.

Dichloromethane, (*methylene chloride*), CH_2Cl_2, is a colorless liquid (*d.* 1.337) having a chloroform-like odor. Its vapor, or saturation, pressure over the range of −20° to +16°C. may be represented by the formula

$$\log_e p_s = 17.89600 - (4.1191 \times 10^3/T) + (3.573 \times 10^6/T^2) - (5.386 \times 10^7/T^3)$$

in which p_s is the saturation pressure in mm. of mercury, and T is the temperature in degrees absolute.[15] Calculations, according to this formula, indicated its boiling point to be 40.18°C., critical temperature 216°C., and critical pressure 49.7 kg. per sq. cm. At 460°C., in the presence of a large excess of steam and tin phosphate on pumice (as a catalyst), it is hydrolyzed to give a 75 per cent yield of formaldehyde.[16] When mixed with methyl chloride and the mixture hydrolyzed under the same conditions, methylene chloride reacts to the extent of 90 per cent while only 30 per cent of the methyl chloride is affected. Also, it has been pointed out that the dichloride may be condensed with formaldehyde to furnish chloroacetaldehyde.[17] The reaction was effected at 300°C. in the presence of sulphuryl chloride, which served as a promoter.

Admixed with other solvents (e.g., naphtha or butyl alcohol) this dichloromethane has been suggested as a dewaxing agent for lubricating oils.[18] It may be employed also as a constituent of compositions for the preparation of films from acetylcellulose,[19] and for cleaning paints, varnishes or enamels.[20] When mixed with benzene it furnishes a composite solvent applicable for extraction of lecithin and fat from corn or soy beans.[21] Collier[22] points out that methylene chloride can be used with safety only when ventilation is adequate. Development of acidity and corrosion of metals by this dichloride are inhibited by incorporation of 0.5 to 2 per cent of an unsaturated hydroaromatic compound, e.g., pinene.[23]

Chloroform, $CHCl_3$, because of its well-known applications as an anesthetic,[24] solvent and extraction agent, is an important chlorinated derivative of methane. It is also miscible with many organic liquids. Bottecchia[25] reports that when mixed with nitrobenzene maximum contraction occurs with 50 per cent (by weight) of chloroform at −16°C. or with 65 per cent at 40°C. The greatest expansion (between 16° and 40°C.) of chloroform-benzene mixtures is obtained with one containing 27 per cent (by weight) of the chloro-hydrocarbon.[26] When mixed with butane and ethyl ether, chloroform is reported to furnish an effective dielectric for electric cables.[27] Zappi and Degiorgi[28] believe that the hydrogen (in chloroform) is in an active state, and that the structure of this chloro-derivative may be represented by the coordination formula $(CCl_3)H$. On the other hand, the hydrogens in bromoform and iodoform are, respectively, 50 and 3 per cent active, thus indicating a mixture of coordinated and normal structures.

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[15] S. Sugawara. *J. Soc. Mech. Engrs., Tokyo,* 1934, **37**, 491; *Chem. Abs.*, 1935, **29**, 16; *Brit. Chem. Abs.* **A**, 1935, 437.

[16] A. Abkin and S. Medvedev, *loc. cit.*

[17] German P. 629,827, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 6036.

[18] P. J. Carlisle, U. S. P. 1,978,010, Oct. 23, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 892; *J. Inst. Pet. Tech.*, 1935, **21**, 27A; *Chem. Abs.*, 1935, **29**, 335. Canadian P. 338,604, 1934, to Canadian Industries Ltd.; *Chem. Abs.*, 1934, **28**, 2177.

[19] French P. 769,525, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 599. *Cf.* A. Ascherl and W. Gruber, German P. 627,729, 1936, to Alexander Wacker Gesellschaft fur elektrochemische Industrie G.m.b.H.; *Chem. Abs.*, 1936, **30**, 6195. Also A. Lubke and R. Muller, German P. 629,589, 1936, to C. F. Boehringer & Soehne G.m.b.H.; *Chem. Abs.*, 1936, **30**, 6194.

[20] A. Abraham and M. L. A. Philippon, French P. 780,494, 1935; *Chem. Abs.*, 1935, **29**, 5954. *Cf.* F. Faucutt and T. M. Herbert, British P. 446,147 1936; *Chem. Abs.*, 1936, **30**, 6856.

[21] M. Reznichenko and A. Poptzova, *Sci. Inst. Cereal Research (Moscow)*, 1934, **13**, 35; *Chem. Abs.*, 1935, **29**, 543.

[22] H. Collier, *Lancet,* 1936, **1**, 594; *Chem. Abs.*, 1936, **30**, 3540; *Brit. Chem. Abs.* **B**, 1936, 430.

[23] G. Braun, U. S. P. 1,966,881, July 17, 1934, to P. J. Sartain, C. R. Fassnacht and R. C. Schwoerer; *Brit. Chem. Abs.* **B**, 1935, 434; *Chem. Abs.*, 1934, **28**, 5904.

[24] The addition of a small proportion of chloroform to ether is recommended by M. Watanabe, Japanese P. 109,894, 1935, to The Minister of War; *Chem. Abs.*, 1935, **29**, 4902.

[25] G. Bottecchia, *Atti ist. Veneto,* 1932-33, **92**, 9; *Chem. Abs.*, 1934, **28**, 3287; *Brit. Chem. Abs.* **A**, 1933, 1110.

[26] G. Bottecchia, *Atti ist. Veneto,* 1934, **93**, 567; *Chem. Abs.*, 1936, **30**, 4062.

[27] French P. 796,141, 1936, to Compagnie generale d'electricite; *Chem. Abs.*, 1936, **30**, 5685.

[28] E. V. Zappi and H. Degiorgi *Anales asoc. quim. Argentina,* **23**, 14; *Chem. Abs.*, 1935, **29**, 7272. *Cf.* G. Urbain, *Bull. soc. chim.*, 1932, **51**, 853; *Chem. Abs.*, 1932, **26**, 5508. A. Tchakirian, *Bull. soc. chim.*, 1932, **51**, 846; *Chem. Abs.*, 1932, **26**, 5508.

According to Rozeboom,[29] chloroform may be distinguished from carbon tetrachloride in the following manner. A small crystal of iodine is dissolved in the liquid and then a few milligrams of papaverine hydrochloride added. If the solvent is carbon tetrachloride no reaction occurs, otherwise the alkaloid salt dissolves and the violet color of the solution is changed to a yellowish red. Another test comprises the reduction of boiling Fehling's solution with chloroform.[30] Also, when a drop of carbon tetrachloride is heated in a loosely corked test tube (flameless combustion) it is converted into phosgene and chlorine, and the latter detected by potassium iodide and starch. Madsen[31] has developed a method for showing the presence of carbon tetrachloride in chloroform. Twenty grams of the liquid are carefully evaporated until 0.5 cc. remains. This is shaken with 150 times its weight of water. A distinct opalescence indicates 1 per cent of the tetrachloride; if none of the latter is present, complete dissolution occurs in 2 minutes.

Fractionation of primary tars with chloroform furnishes neutral oils, resinous bodies and phenols.[32] Danaila and Soare[33] report that the only method, which is technically and economically advantageous, for making chloropicrin is the nitration of trichloromethane. They obtained a 58 per cent yield by heating equal volumes of chloroform and nitric acid (*d.* 1.52) at 140-150°C. for 2 hours under pressure. The action of Friedel-Crafts condensing agents upon chloroform has been investigated.[34] It was stated that the trichloride will react with *p*-dichlorobenzene in the presence of aluminum chloride. When solvents are excluded from the reaction zone and the temperature maintained at 20°C. the product is said to be tri-(2,5-dichlorophenyl) methane. When admixed with dimethyl ether and conducted over alumina gel at 280°C., chloroform is said to furnish methyl chloride.[34a]

The preparation of chloroform-d (deuteriochloroform) from chloral deuterate and sodium deutroxide is described by Breuer.[35] Also, it has been suggested that chloral (trichloroacetaldehyde) be treated with calcium oxide and deuterium oxide (heavy water) to furnish heavy chloroform.[36] At 732 mm. this trichloro compound boiled 0.5°C. higher than its lighter analogue. Some of the other physical properties of these two trichloro derivatives are given in Table 153.

TABLE 153.—*Physical Properties of Chloroform and Chloroform-d.*

	Chloroform	Chloroform-d
M.P.	−63 77° to −63.33°C.	−64.69° to −64.15°C.
F.P.	−63 49° to −63 92°C.	−64.12°C.
n_D^{20}	1.4450	1.4450
d_4^{20}	1 4880	1 5004

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[29] J. Rozeboom, *Pharm. Weekblad*, 1935, **72**, 689; *Chem. Abs.*, 1935, **29**, 5386; *Brit. Chem. Abs.* **A**, 1935, 958.

[30] N. Schoorl, *Pharm. Weekblad.*, 1935, **72**, 751; *Brit. Chem. Abs.* **A**, 1935, 958; *Chem. Abs.*, 1935, **29**, 5986.

[31] E. H. Madsen, *J. Pharm. Chim.*, 1935, **21** (8), 246; *Brit. Chem. Abs.* **B**, 1935, 442; *Chem. Abs.*, 1935, **29**, 4899.

[32] Ya. I. Chulkov, *Coke and Chem.* (*U.S.S.R.*), 1933, **3**, No. 8, 18; *Brit. Chem. Abs.* **B**, 1936, 6; *Chem. Abs.*, 1935, **29**, 3140.

[33] N. Danaila and A. Gh. Soare, *Bull. chim. soc. romane chim.*, 1932, **35**, 53; *Chem. Abs.*, 1934, **28**, 3712; *Brit. Chem. Abs.* **A**, 1934, 508.

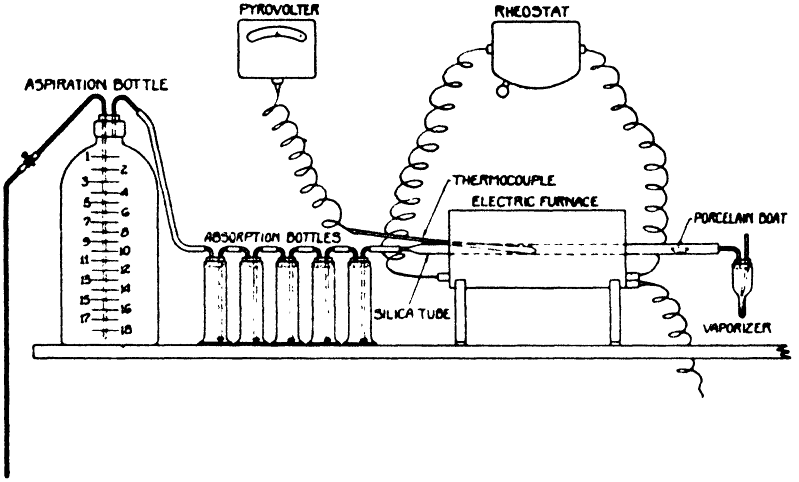
[34] S. D. Wilson and H. T. Huang, *J. Chinese Chem. Soc.*, 1936, **4**, 142; *Brit. Chem. Abs.* **A**, 1936, 976; *Chem. Abs.*, 1936, **30**, 8192.

[34a] French P. 799,582, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 7585.

[35] F. W. Breuer, *J.A.C.S.*, 1935, **57**, 2236; *Chem. Abs.*, 1936, **30**, 78.

[36] R. Truchet, *Compt. rend.*, 1936, **202**, 1997; *Chem. Abs.*, 1936, **30**, 6643; *Brit. Chem. Abs.* **A**, 1936, 1090.

Carbon tetrachloride, CCl_4, is a heavy, colorless liquid (sp. gr. 1.595) boiling at 76.7°C. at 760 mm. As previously mentioned it can be prepared by chlorination of methane. Another method consists in saturating carbon disulphide with chlorine and warming the mixture to 40-60°C.[37] Catalysts such as iron, manganese, chromium or silicon may be used. A 68-80 per cent yield is reported to be obtained by passage of sulphur dichloride over carbon at 1000°C.[38] Weiler[39] reports that the volatile reaction products from the exhaustive chlorination of coal for 6 days at 200°C. consisted of carbon tetrachloride, hexachloroethane and hexachlorobenzene. According to Davies[40] the dielectric constants for the tetrachloride at 20°C. and 25°C. are 2.236 and 2.227, respectively. He recommends it as a secondary standard for calibrations. The crystalline forms of both the tetrachloride and tetrabromide are bimolecular while those for ethylene chloride or bromide are tetramolecular.[41]



Courtesy Industrial and Engineering Chemistry

FIG. 154.—Apparatus for Quantitative Determination of Carbon Tetrachloride Vapor. (J. C. Olsen, H. F. Smyth, Jr., G. E. Ferguson and L. Scheflan)

Carbon tetrachloride and other chlorinated hydrocarbons, particularly when moist, slowly undergo decomposition in contact with metals such as iron, zinc, copper or Monel metal. Numerous agents have been suggested as stabilizers or inhibitors of such action and include mercaptans,[42] e.g., butyl mercaptan, ethyl acetate,[43] natural resins,[44] such as gum mastic or rosin, alkyl or aryl cyanamides,[45] thiocarbamides,[46] ureides,[46a] hexamethylenetetramine[47] and ethyl cyanide.[48]

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[37] German P. 604,347, 1934, to Firma Stabilimenti di Rumianca; *Chem. Abs.*, 1935, **29**, 817.

[38] L. S. Maiofis, G. M. Shusterovich and N. N. Bibikov, *Trans. State Inst. Applied Chem. (U.S.S.R.)*, 1935, **24**, 119; *Chem. Abs.*, 1935, **29**, 7272.

[39] J. F. Weiler, *J.A.C.S.*, 1936, **58**, 1112; *Chem. Abs.*, 1936, **30**, 6165.

[40] R. M. Davies, *Phil. Mag.*, 1936, **21**, 1; *Chem. Abs.*, 1936, **30**, 2062; *Brit. Chem. Abs.* **A**, 1936, 271.

[41] E. I. K. Verstraete, *Bull. soc. chim. Belg.*, 1934, **43**, 513; *Chem. Abs.*, 1935, **29**, 725; *Brit. Chem. Abs.* **A**, 1935, 156.

[42] British P. 401,210, 1933, to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1934, 53; *Chem. Abs.*, 1934, **28**, 2363.

[43] P. S. Brailler, U. S. P. 2,002,168, May 21, 1934, to Niagara Smelting Corp.; *Chem. Abs.*, 1935, **29**, 4381; *Brit. Chem. Abs.* **B**, 1936, 683.

[44] L. C. Stewart and L. de Pree, U. S. P. 1,971,318, Aug. 21, 1934, to Dow Chemical Co.; *Chem. Abs.*, 1934, **28**, 6443; *Brit. Chem. Abs.* **B**, 1935, 715.

[45] E. C. Missbach, U. S. P. 2,043,257, June 9, 1936, to Stauffer Chemical Co.; *Chem. Abs.*, 1936, **30**, 5240.

The tendency of carbon tetrachloride to undergo decomposition when mixed with moist air has been made the basis of a quantitative method of determining the tetrachloride.[49] The apparatus consists of a glass funnel connected to an electric furnace through a silica tube. At the outlet of the latter are placed a series of absorption bottles containing aqueous caustic soda and an aspiration bottle (see Fig. 154). In the procedure a weighed amount of carbon tetrachloride is placed in the funnel. The furnace is then heated to 1000-1100°C. and a mixture of vaporized carbon tetrachloride and moist air drawn through, forming hydrogen chloride and carbon dioxide.

$$CCl_4 + 2H_2O \longrightarrow CO_2 + 4HCl$$

To insure the presence of a sufficient quantity of water a small porcelain boat containing water is placed at the entrance to the furnace. As the gases leave the furnace, the hydrogen chloride is absorbed in a known volume of the aqueous caustic soda. The excess hydrochloric acid may then be determined by titration of these solutions with silver nitrate.

Uses suggested for carbon tetrachloride are, as a dewaxing[50] and refining agent,[51] either alone or blended with other halogenated hydrocarbons; in the processing of lubricating oils; as a decarbonizing reagent for internal combustion engines;[52] in the preparation of sand molds;[52a] as a cleaning agent for metals;[52b] in the preparation of cosmetics;[53] and mixed with wax-like ketones in the manufacture of waxing and polishing compositions for automobiles, furniture and floors.[54] A die lubricant, to be employed in the extrusion of magnesium alloys, is made by suspending finely-ground graphite in the tetrachloride.[55] The production of chloral is said to be effected by the interaction of carbon tetrachloride and formaldehyde.[56] The condensation may be carried out at temperatures in the range 200-500°C. and at pressures from 20 to 200 atmospheres. Passage of the vapors of tetrachloromethane through granular carbon at 600-1500°C. (best at 800-900°C.) furnishes tetra- and hexachloroethane.[57] These may be separated by fractional distillation, or the mixture subjected to chlorination to increase the yield of the hexachloro compound. Also, a phthalyl chloride is stated to be furnished by admixing phthalic anhydride and carbon tetrachloride and heating the resulting composite to 250-280°C.[58] A resin applicable in molding is reported to be formed by the reaction of petrolatum with carbon tetrachloride in the presence of aluminum chloride.[58a] In one example 100 g. of petrolatum were admixed with a like amount of anhydrous aluminum chloride and heated to 80°C. Carbon tetrachloride (100 g.) was then incorporated and the mass heated until all gaseous products were evolved. In this manner 94 g. of a resin which contained 3 to 13 per cent of chlorine was said to be formed.

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[46] E. C. Missbach, U. S. P. 2,043,258, June 9, 1936, to Stauffer Chemical Co.; *Chem Abs.*, 1936, **30**, 5240.

[46a] E. C. Missbach, U. S. P. 2,069,711, Feb. 9, 1937, to Stauffer Chemical Co.

[47] E. C. Missbach, U. S. P. 2,043,259, June 9, 1936, to Stauffer Chemical Co.; *Chem. Abs.*, 1936, **30**, 5240.

[48] E. C. Missbach, U. S. P. 2,043,260, June 9, 1936, to Stauffer Chemical Co.; *Chem. Abs.*, 1936, **30**, 5240.

[49] J. C. Olsen, H. F. Smyth, Jr., G. E. Ferguson and L. Scheflan, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, *260*; *Chem. Abs.*, 1936, **30**, 5906.

[50] French P. 790,852 and 790,853, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 3223. British P. 446,607, 1936; *Chem. Abs.*, 1936, **30**, 6937. L. C. Kettenring and L. H. Robertson, U. S. P. 2,055,627, Sept. 29, 1936; *Chem. Abs.*, 1936, **30**, 7839.

[51] French P. 790,326, 1935, to Vacuum Oil Co. (Soc. anon. francaise); *Chem. Abs.*, 1936, **30**, 3225.

[52] E. Bagnall-Bull, British P. 397,849, 1933; *Chem. Abs.*, 1934, **28**, 1843.

[52a] A. Y. Gregory and E. E. Seeley, U. S. P. 2,056,048, Sept. 29, 1936; *Chem. Abs.*, 1936, **30**, 8137.

[52b] G. Wolff, German P. 635,757, 1936, to Alexander Wacker Ges. für elektrochemische Industrie G.m.b.H.; *Chem. Abs.*, 1937, **31**, 580.

[53] B. Hauck (nee Hosp), German P. 622,372, 1935; *Chem. Abs.*, 1936, **30**, 1524.

[54] A. W. Ralston and C. W. Christensen, U. S. P. 2,033,544, Mar. 10, 1936, to Armour & Co.; *Chem. Abs.*, 1936, **30**, 3134.

[55] R. T. Wood, U. S. P. 1,946,121, Feb. 6, 1934, to Magnesium Development Corp.; *Brit. Chem. Abs.* **B**, 1935, 274.

[56] P. K. Frolich and P. J. Wiezevich, U. S. P. 2,042,303, May 26, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 4871.

[57] C. J. Strosacker and C. C. Schwegler, U. S. P. 1,930,350, Oct. 10, 1933, to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1934, 750; *Chem. Abs.*, 1934, **28**, 180.

Because of its non-inflammable properties tetrachloromethane has found application in the preparation of insecticidal sprays, dry-cleaning compositions and fire-extinguishers. A spray for use as an insecticide in airplanes consists of 1 part of pyrethrum extract in kerosene and 4 parts of carbon tetrachloride.[59] Badertscher[60] suggests suspending talc in such preparations, so that after spraying plants the latter become coated with a fine insecticidal dust.

Dry-cleaning liquids may comprise the tetrachloride incorporated with another halogenated hydrocarbon such as ethylene chloride,[61] or blends of petroleum naphtha with sufficient carbon tetrachloride or acetylene tetrachloride,[62] or mixtures of these chlorides,[63] to render the composition non-flammable. The addition of a small proportion of an oil-soluble alkali sulphonate, called mahogany soap, to a petroleum naphtha-carbon tetrachloride blend has been suggested to increase the detergent properties of the cleaning fluid.[64] To eliminate fire and explosion hazards connected with the handling of hexane, heptane, octane, gasoline and naphtha, Jones and Kennedy[65] recommend incorporation of at least 70 per cent by volume of tetrachloride. With pentane 80 per cent is required. Although recovery of dry-cleaning solvent by distillation is the usual practice, Stout and Tillman[66] point out that continuous adsorption and filtration processes have certain advantages as for instance reduction in cost and time required for reclamation. They state that it is necessary to remove saponifiable materials and acids, but that the presence of mineral oils (in moderate concentrations) in the fluids is helpful in cleaning operations. With an azeotropic mixture of carbon tetrachloride and ethylene chloride, it was found that activated carbon and magnesium oxide removed saponifiable oils and acids, and that silica gel eliminated both saponifiable and unsaponifiable substances.

The use of carbon tetrachloride, either alone or incorporated with other halogenated hydrocarbons, in fire-extinguishers is well-known.[67] The development of phosgene during the application of this liquid to fires has been measured by Yant,

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[58] J. R. Mares, U. S. P. 2,051,096, Aug. 18, 1936, to Monsanto Chemical Co.; *Chem Abs.*, 1936, **30**, 6762.

[58a] H. G. Berger, U. S. P. 2,043,825, June 9, 1936, to Socony-Vacuum Oil Co; *Chem. Abs.*, 1936, **30**, 5327.

[59] C. L. Williams and W. C. Dressen, *U. S Pub. Health Repts.*, 1935, **50**, 1401; *Chem. Abs.*, 1936, **30**, 188.

[60] A. E. Badertscher, U. S. P. 1,940,899, Dec. 26, 1933, to McCormick & Co.; Inc.; *Brit. Chem. Abs.* **B**, 1935, 74; *Chem. Abs.*, 1934, **28**, 1460.

[61] A. Mohn, U. S. P. 1,940,688, Dec. 26, 1933, to Rhodes-Perry Martin, Inc.; *Brit. Chem. Abs.* **B**, 1935, 59; *Chem. Abs.*, 1934, **28**, 1552.

[62] M. A. Youtz, U. S. P. 2,031,144 and 2,031,145, Feb. 18, 1936, to Standard Oil Co. of Indiana; *Chem. Abs.*, 1936, **30**, 2408; *Brit. Chem. Abs.* **B**, 1937, 16. *Cf.* A. C. Loges, U. S. P. 2,015,943, Oct. 1, 1935; *Brit. Chem. Abs.* **B**, 1936, 1058; *Chem. Abs.*, 1935, **29**, 8393.

[63] J. J. Grebe, S. M. Stoesser and L. E. Mills, U. S. P. 1,989,478, Jan. 29, 1935, to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1936, 90; *Chem. Abs.*, 1935, **29**, 2000.

[64] G. L. Parkhurst, U. S. P. 2,053,007, Sept. 1, 1936, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1936, **30**, 7362.

[65] G. W. Jones and R. E. Kennedy, *Bur. Mines, Inf. Circ. No.*, 6805, 1934; *Chem. Abs.*, 1935, **29**, 1985; *J. Inst. Pet. Tech.*, 1935, **21**, 181A.

[66] L. E. Stout and A. B. Tillman, *Ind. Eng. Chem.*, 1936, **28**, 22; *Brit. Chem. Abs.* **B**, 1936, 315; *Chem. Abs.*, 1936, **30**, 1237. The use of carbon tetrachloride in various dry-cleaning processes is discussed by D. H. Killeffer, *Ind. Eng. Chem.*, 1936, **28**, 640; *Chem. Abs.*, 1936, **30**, 4678.

[67] See for example, J. Neumann, British P. 437,156, 1935; *Chem. Abs.*, 1936, **30**, 3128. F. Stowener and J. Kine, German P. 608,037, 1935, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech.*, 1935, **21**, 216A; *Chem. Abs.*, 1935, **29**, 2634. A review of various chemical fire extinguishers has been given by F. Boye, *Chem.-Ztg.*, 1935, **59**, 155, 513; *Brit. Chem. Abs.* **B**, 1935, 433; *Chem. Abs.*, 1936, **30**, 3118.

Olsen, Storch, Littlefield and Scheflan.[68] These investigators observed that in the case of fires with excelsior (as the inflammable material) 4 to 92 parts per million (by volume) of phosgene were formed, an average value being about 23.6 parts per million. However, when carbon tetrachloride was dropped onto a red-hot iron beam the proportion of phosgene rose to 119 parts per million. Malzac[69] suggests that the fire-extinguishing liquid may be stabilized and the formation of carbonyl chloride and hydrogen chloride prevented by incorporation of aniline. The mechanism of the extinguishing power of carbon tetrachloride on coal-gas flames was investigated by Dufraisse and LeBas.[70] They believe the action to be complex, a combination of dilution of the surrounding atmosphere and consequent cooling, a definite antioxygenic influence, and a combustion-supporting effect due to hydrogen (of the combustible material) reacting with the chlorine in preference to oxygen.

The toxic properties of carbon tetrachloride have been studied by Lehnherr,[71] Ciaravino,[72] Löwy,[73] Young,[73a] and Maiofis, Shusterovich and Bibikov.[74] According to Okunevskii[75] the efficiency of insecticides depends upon the lethal concentration of the toxic material and the rate at which it is capable of producing that concentration. Liquids which are particularly applicable for this purpose are carbon tetrachloride and benzene, since they are sufficiently volatile at ordinary temperatures. The use of this tetrachloride as a parasiticide was investigated by Ackert and Graham.[76].

PREPARATION OF CHLOROFLUOROMETHANES

These mixed halogenated hydrocarbons, particularly dichlorodifluoromethane, are usually prepared by the action of antimony trifluoride on carbon tetrachloride, using antimony pentachloride as a catalyst.[77] The reaction is represented as

$$3CCl_4 + 2SbF_3 \xrightarrow{SbCl} 3CCl_2F_2 + 2SbCl_3$$

McNary[78] points out that the presence of a small proportion of antimony dichlorotrifluoride increases the speed and the efficiency of the reaction. This latter compound can be obtained by the interaction of chlorine with the metallic fluoride at temperatures above 70°C. Lead or zinc fluoride may be employed in a similar manner. Another procedure for effecting fluorination comprises treatment of the chloro-hydrocarbon, carbon tetrachloride or tetrachloroethane[79] with antimony trifluoride and simultaneously introducing chlorine into the reaction zone. In the procedure carbon tetrachloride was pumped to a reaction chamber containing antimony trifluoride. At the same time chlorine was introduced into the chamber. The latter was heated by passage of steam through a jacket which surrounded it. During the time of interaction the temperature was maintained at 60-65°F. and the pressure at 55 pounds gage (69.7 pounds per sq. in.). The gaseous products, including dichlorodifluoromethane, trichlorofluoromethane and unreacted carbon tetrachloride were then led to a dephlegmator, where the trichloro and tetrachloro compounds were condensed and returned to the fluorinating chamber, while difluorodichloromethane was washed with aqueous caustic soda, dried with concentrated sulphuric acid, and condensed. Also, it has been suggested that methylene chloride be reacted with antimony trifluoride.[80] In this instance antimony pentachloride rather than chlorine was incorporated in the reaction zone. When the temperature was maintained at 80°F. and the pressure at 130 pounds gage (144.7 pounds per sq. in.) difluoromethane was stated to be the main product. The di-

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[68] W. P. Yant, J. C. Olsen, H. H. Storch, J. B. Littlefield and L. Scheflan, *Ind Eng. Chem Anal Ed.*, 1936, **8**, 20; *Chem. Abs.*, 1936, **30**, 1458; *Brit. Chem. Abs.* **B**, 1936, 232.

[69] A. C. Malzac, French P. 789,462, 1935; *Chem. Abs.*, 1936, **30**, 1905.

[70] C. Dufraisse and I. LeBas, *Compt rend.*, 1936, **202**, 227; *Chem. Abs.*, 1936, **30**, 2004. *Brit. Chem. Abs.* **B**, 1936, 482. *Compt. rend.*, 1934, **199**, 75; *Chem. Abs.*, 1934, **28**, 5672; *Brit. Chem. Abs.* **B**, 1934, 815

[71] E. R. Lehnherr, *Arch. Internal Med.*, 1935, **56**, 98; *Chem. Abs.*, 1935, **29**, 6648; *Brit. Chem. Abs.* **A**, 1935, 1276.

[72] E. Ciaravino, *Boll. chim farm.*, 1935, **74**, 741; *Chem. Abs.*, 1936, **30**, 409; *Brit. Chem. Abs.* **A**, 1935, 1533.

[73] J. Löwy, *Arch. Gewerbepath. Gewerbehyg.*, 1935, **6**, 157, *Chem. Abs.*, 1936, **30**, 1436.

[73a] C. Young, *Can. Med. Assoc. J.*, 1936, **35**, 419; *Chem Abs.*, 1936, **30**, 8390.

[74] L. S. Maiofis, G. M. Shusterovich and N. N. Bibikov, *Trans State Inst. Applied Chem. (U.S.S.R.)*, 1935, **24**, 128; *Chem. Abs.*, 1935, **29**, 7272. *Cf.* H. F Smyth, H. F. Smyth, Jr., and C. P. Carpenter, *J. Ind. Hyg. Toxicol.*, 1936, **18**, 277; *Brit. Chem. Abs.* **A**, 1936, 893; *Chem. Abs.*, 1936, **30**, 6844.

[75] I. Okunevskii and V. Khakhaeva, *Med. Parasitology & Parasitic Diseases (Moscow)*, 1934, **3**, 82; *Chem. Abs.*, 1936, **30**, 2664.

[76] J. E. Ackert and G. L. Graham, *Poultry Sci.*, 1935, **14**, 228; *Chem. Abs.*, 1936, **30**, 1869; *Brit. Chem. Abs.* **B**, 1936, 38.

[77] For a review of these methods see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, **1934**. Also F. H. Reed and G. C. Finger, *Chem. Industries*, 1936, **39**, 577; *Chem. Abs.*, 1937, **31**, 1167. *Trans. Illinois State Acad Sci.*, 1935, **28** (2), 129; *Chem. Abs.*, 1936, **30**, 3949. An apparatus for effecting such reactions is described by T. Midgley, Jr., A. L. Henne and R. R. McNary, Canadian P. 355,052, 1935, to Frigidaire Corp.; *Chem. Abs.*, 1936, **30**, 2579. See also L. C. Holt, M. A. Youker and R. F. Laird, U. S. P. 2,058,453, Oct. 27, 1936, to Kinetic Chemicals, Inc.; *Chem. Abs.*, 1937, **31**, 115.

[78] R. R. McNary, Canadian P. 350,603, 1935, to Frigidaire Corp.; *Chem. Abs.*, 1935, **29**, 5123. A. L. Henne, U. S. P. 1,978,840, Oct. 30, 1934, to General Motors Corp.; *Chem. Abs.*, 1935, **29**, 175; *Brit. Chem. Abs.* **B**, 1935, 839.

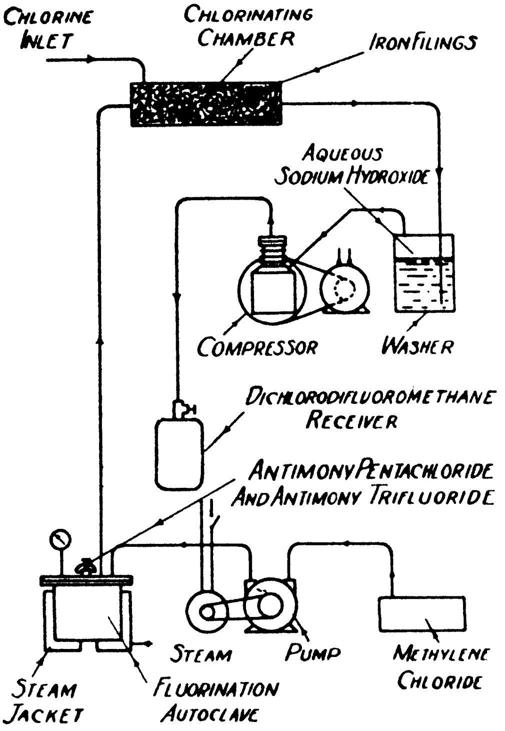

FIG. 155. Flow Diagram for Manufacture of Dichlorodifluoromethane, Involving Intermediate Formation of Difluoromethane. (T. Midgley, Jr., A. L. Henne and R. R. McNary)

fluoride was then conducted, together with chlorine, through a tube packed with iron filings (see Fig. 155). In this manner, dichlorodifluoromethane was reported to be secured.

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[79] A. L. Henne, U. S. P. 1,990,692, Feb. 12, 1935, to General Motors Corp.; *Brit. Chem. Abs.* **B**, 1936, 88; *Chem. Abs.*, 1935, **29**, 2174.

[80] T. Midgley, Jr., A. L. Henne and R. R. McNary, U. S. P. 2,007,208, July 9, 1935, to General Motors Corp.; *Chem. Abs.*, 1935, **29**, 5459; *Brit. Chem. Abs.* **B**, 1936, 632.

In place of the above-mentioned metallic fluorides, hydrogen fluoride (mixed with a hydrogen halide) may be employed as the fluorinating agent and activated carbon as the catalyst.[81] When operations are carried out in the vapor phase at slightly elevated temperatures (110-170°C.) in the absence of contact materials, aralkyl halides are converted into fluorides.[82] An example of this is the preparation of benzotrifluoride from the corresponding trichloride. The latter procedure is applicable also to the transformation of trifluorotrichloroethane into pentafluorochloroethane.[83] However, other catalysts which may be used with hydrogen fluoride (and chloromethanes) include antimony tri- and pentachloride,[84] antimony

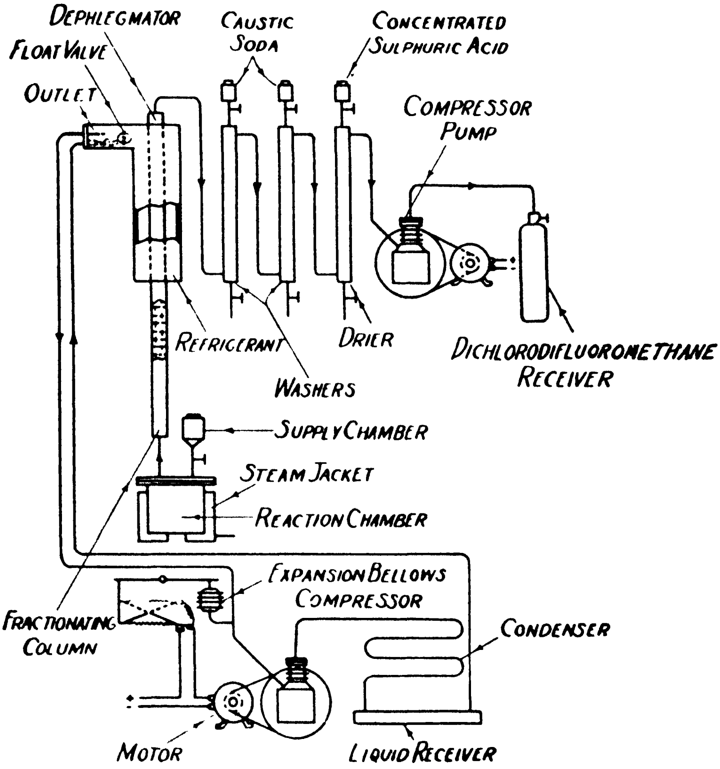

FIG. 156—Sketch of Method for Making Dichlorodifluoromethane by Direct Fluorination of Carbon Tetrachloride. (T. Midgley, Jr., A. L. Henne and R. R. McNary)

fluorochlorides,[85] a mixture of phosphorus pentachloride and antimony pentachloride,[86] and ferric chloride.[87] For example, carbon tetrachloride, antimony trifluoride and antimony pentachloride may be admixed in a reaction vessel at atmospheric pressure. The gaseous products are then conducted to a dephlegmator which is cooled by a refrigerant to —20°C. In this manner all partially fluorinated and unreacted hydrocarbons are condensed and returned to the fluorinating chamber. The dichlorodifluoromethane is led from the top of the dephlegmator, washed and compressed. Silicon tetrafluoride[88] and bromine trifluoride[89] have also been proposed as fluorinating agents.

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[81] British P. 428,445, 1933, to Kinetic Chemicals, Inc.; *Brit. Chem. Abs.* **B**, 1935, 664; *Chem. Abs.*, 1935, **29**, 6901. *Cf.* H. W. Daudt and M. A. Youker, U. S. P. 2,062,743, Dec. 1, 1936; *Chem. Abs.*, 1937, **31**, 700.

[82] L. C. Holt and E. L. Mattison, U. S. P. 1,967,244, July 24, 1934, to Kinetic Chemicals, Inc.; *Brit. Chem. Abs.* **B**, 1935, 616; *Chem. Abs.*, 1934, **28**, 5831. British P. 428,361, 1935, to Kinetic Chemicals, Inc.; *Chem. Abs.*, 1935, **29**, 6605; *Brit. Chem. Abs.* **B**, 1935, 664.

[83] H. W. Daudt and M. A. Youker, U. S. P. 2,005,706, June 18, 1935, to Kinetic Chemicals, Inc.; *Chem. Abs.*, 1935, **29**, 5123.

[84] H. W. Daudt and M. A. Youker, U. S. P. 2,005,705, 2,005,707, 2,005,708, 2,005,709, 2,005,710,

Courtesy Kinetic Chemicals, Inc.

FIG. 157.—Dichlorodifluoromethane Plant, Showing Storage Racks.

Another procedure for the manufacture of chlorofluoromethanes consists in conducting the vapors of carbon tetrachloride over calcium fluoride at a temperature of 350°C. or higher.[90] A salt of antimony other than the fluoride (e.g., the

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2,005,711, June 18, 1935, to Kinetic Chemicals, Inc.; *Chem. Abs.*, 1935, **29**, 5123. L. C. Holt and E. L. Mattison, U. S. P. 2,005,712, June 18, 1935, to Kinetic Chemicals, Inc.; *Chem. Abs.*, 1935, **29**, 5123. T. Midgley, Jr., A. L. Henne and R. R. McNary, U. S. P. 1,930,129, Oct. 10, 1933, to Frigidaire Corp.; *Brit. Chem. Abs.* **B**, 1934, 750; *Chem. Abs.*, 1934, **28**, 179.

[85] H. W. Daudt, M. A. Youker and H. H. Reynolds, U. S. P. 2,024,095, Dec. 10, 1935, to Kinetic Chemicals, Inc.; *Chem. Abs.*, 1936, **30**, 1067; *Brit. Chem. Abs.* **B**, 1936, 1192.

[86] L. C. Holt and E. L. Mattison, U. S. P. 2,005,712, June 18, 1935, to Kinetic Chemicals, Inc.; *Chem. Abs.*, 1935, **29**, 5123.

[87] H. W. Daudt and M. A. Youker, U. S. P. 2,005,707, June 18, 1935, to Kinetic Chemicals, Inc.; *Chem. Abs.*, 1935, **29**, 5123. *Cf.* H. W. Daudt and E. L. Mattison, U. S. P. 2,004,931, June 18, 1935, to Kinetic Chemicals, Inc.; *Chem. Abs.*, 1935, **29**, 5123.

[88] A. L. Henne, U. S. P. 1,973,069, Sept. 11, 1934, to General Motors Corp.; *Chem. Abs.*, 1934, **28**, 6723.

[89] H. S. Nutting and P. S. Petrie, U. S. P. 1,961,622, June 5, 1934, to Dow Chemical Co.; *Chem. Abs.*, 1934, **28**, 4746; *Brit. Chem. Abs.* **B**, 1935, 347.

[90] B. S. Lacy, Canadian P. 353,775, 1935, to Canadian Industries Ltd.; *Chem. Abs.*, 1936, **30**, 2199.

sulphate) may be incorporated with the calcium compound.[91] Slow passage of chloroform vapors over mixed calcium and silver fluorides at 100°C. yielded about 57 per cent of monofluorodichloromethane.[92] At 250°C. approximately 48 per cent of difluoromonochloromethane is obtained, and at 340°C. only 10 per cent of fluoroform is secured. Lead fluoride at 500°C. gave only a small proportion of monofluorodichloromethane. Croco[93] observed that treatment of fluorotrichloromethane with aluminum chloride (at 45°C.) yielded difluorodichloromethane and carbon tetrachloride. Similarly, fluorodichloromethane furnished difluoromonochloromethane.

It is interesting to note that trichlorofluoromethane and dichlorodifluoromethane may be prepared from carbon disulphide.[94] Thus, the latter substance was combined with hydrogen fluoride in the presence of antimony pentachloride and free chlorine. The resulting compound was said to contain a mixture of the two fluorine derivatives mentioned above.

Acidic impurities may be eliminated from fluorochloro derivatives by the action of an amine, such as aniline or triethanolamine.[95] The refined product afterwards is separated by fractional distillation.

Iodoform, mercurous fluoride and calcium fluoride (in the proportions of 20 : 33.4 : 40) heated to 80-150°C. yielded a mixture of fluoroform, iododifluoro- and di-iodofluoromethane which could be separated by distillation.[96] The di- and trifluoro derivatives were gases at room temperature while the monofluoride was a liquid. Some of the physical constants of these compounds are given in Table 154.

TABLE 154.—*Physical Constants of the Fluorine Derivatives of Iodoform.*

Compound	B.P.	M.P.	*d* (at liquid air temperature)
CHI_2F	100.3°C.	−34.5°C.	3.604
$CHIF_2$	21.6°C.	−122.0°C.	3.238
CHF_3	−84.4°C.	−160.0°C.	1.935

Fluoroform appeared to be the most stable as it was not decomposed on heating to 1150°C. It was not attacked by nitric acid (alone or mixed with sulphuric acid), nitrogen trioxide, or silver nitrate at 150°C. for 14 hours. At temperatures above 175°C. fluoroform was decomposed by the trioxide. When affected by oxidizing agents it was changed into carbonyl fluoride and hydrogen fluoride. Iododifluoromethane was very sensitive to light and air, reacted with silver nitrate and was decomposed by platinized asbestos at 700°C. Diiodofluoromethane also was sensitive to light and air, slowly liberated iodine when warmed, and was almost completely decomposed at 250°C. The diiodo compound yielded ammonium iodide and fluoride on treatment with ammonia. With sodium sulphite in 50 per cent alcohol complete removal of fluorine was observed.

USES OF CHLOROFLUOROMETHANES

Because of their relatively low boiling points, non-flammability and low toxicity these halogenated methanes, especially dichlorodifluoromethane,[97] have been employed as refrigerants. A diester, such as dibutyl phthalate, may be used in conjunction with them as the absorbent.[98] Also, a number of ethers and esters of glycol may be incorporated for the same purpose.[99] Incorporation of a small proportion of a substance which fumes in contact with moisture in the atmosphere (e.g., boron trifluoride, silicon tetrachloride or titanium tetrachloride) serves to detect leaks in the refrigerating system.[100] Another method of detecting leaks in refrigeration machines which contain dichlorodifluoromethane consists of passing

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[91] T. Midgley, Jr. and A. L. Henne, U. S. P. 2,013,062, Sept. 3, 1935, to Frigidaire Corp.; *Chem. Abs.*, 1935, **29**, 6901; *Brit. Chem. Abs.* **B**, 1936, 919.

[92] O. Ruff, O. Bretschneider, W. Luchsinger and G. Miltschitzsky, *Ber.*, 1936, **69**, 299; *Brit. Chem. Abs.* **A**, 1936, 452; *Chem. Abs.*, 1936, **30**, 2869.

[93] C. W. Croco, U. S. P. 1,994,035, Mar. 12, 1935, to Kinetic Chemicals, Inc.; *Chem. Abs.*, 1935, **29**, 2974.

[94] H. W. Daudt, M. A. Youker and H. L. Jones, U. S. P. 2,004,932, June 18, 1935, to Kinetic Chemicals, Inc.; *Chem. Abs.*, 1935, **29**, 5123. *Cf.* J. P. Baxter, British P. 454,577, 1936, to Imperial Chemical Industries Ltd.; *Chem. Abs.*, 1937, **31**, 1045; *Brit. Chem. Abs.* **B**, 1936, 1192; *J. Inst. Pet. Tech.*, 1936, **22**, 553A.

[95] H. W. Daudt, U. S. P. 1,946,195, Feb. 6, 1934, to Kinetic Chemicals, Inc.; *Brit. Chem. Abs.* **B**, 1935, 218; *Chem. Abs.*, 1934, **28**, 2365.

[96] O. Ruff, O. Bretschneider, W. Luchsinger and G. Miltschitzsky, *loc. cit.*

[97] For a comparison of this compound (also known as Freon or F-12) with ammonia as a refrigerant.

Courtesy Kinetic Chemicals, Inc.

Fig. 157A.—View of Plant for Manufacture of Dichlorodifluoromethane.

a sample of air obtained from the vicinity of the suspected leak through a spark between copper electrodes.[101] In this manner a metallic halide which is volatile and has a distinctive color is formed.

Other uses for these fluorine-containing compounds are as fillers for fire extin-

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see G. C. Hodson, *Ice and Cold Storage*, 1936, **39**, 23; *Chem. Abs.*, 1936, **30**, 3283. Trichlorofluoromethane is designated F-11. Its use as a refrigerating medium is described by W. H. Carrier and R. W. Waterfill, U. S. P. 2,041,045, May 19, 1936, to Carrier Engineering Corp.; *Chem. Abs.*, 1936, **30**, 4366. A discussion of the refrigerants in common use is given by J. S. Beamensderfer. *Ind. Eng. Chem.*, 1935, **27**, 1027. *Brit. Chem. Abs.* **B**, 1935, 881; *Chem. Abs.*, 1935, **29**, 6475. See also, Este, *Kälte*, 1936, **12**, 25; *Chem. Abs.*, 1936, **30**, 5075.

[98] J. Fleischer, U. S. P. 2,035,541, Mar. 31, 1936, to General Motors Corp.; *Chem. Abs.*, 1936, **30**, 3286.

[99] G. F. Zellhoefer, U. S. P. 2,040,894, to 2,040,912, May 19, 1936; *Chem. Abs.*, 1936, **30**, 4366.

[100] C. Dantsizen, U. S. P. 1,967,871, July 24, 1934, to General Electric Co.; *Brit. Chem. Abs.* **B**, 1935, 1074; *Chem. Abs.*, 1934, **28**, 5904.

[101] T. Midgley, Jr., U. S. P. 1,990,706, Feb. 12, 1935, to General Motors Corp.; *Brit. Chem. Abs.* **B**, 1936, 815; *Chem. Abs.*, 1935, **29**, 2265.

[102] W. Ursum, German P. 587,932, 1933; *Chem. Abs.*, 1934, **28**, 1826.

[103] A. C. Malzac, French P. 782,140, 1935; *Chem. Abs.*, 1935, **29**, 6984. German P. 630,838, 1936; *Chem. Abs.*, 1937, **31**, 12. See also B. C. Oldham, *Ice and Cold Storage*, 1936, **39**, 85; *Chem. Abs.*, 1937, **31**, 600. L. S. Morse, *Refrigerating Eng.*, 1936, **32**, 17, 86; *Chem. Abs.*, 1936, **30**, 7393.

[104] H. V. Atwell, U. S. P. 2,006,010, June 25, 1935, to Standard Oil Co. of Indiana; *Brit. Chem. Abs.* **B**, 1936, 629; *Chem. Abs.*, 1935, **29**, 5647.

guishers,[102] solvents for cleaning operations,[103] and diluents, either alone[104] or mixed with methyl or ethyl chloride,[105] for the dewaxing of lubricating oils. Getz and Smith[106] suggest charging cream with dichlorodifluoromethane under pressure in a specially constructed siphon bottle and ejecting the mixture as a froth. In this manner whipped cream can be made provided the material initially contains 22 to 36 per cent of fat.

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[105] H. Ramser, U. S. P. 2,009,454, July 30, 1935, to Edeleanu G.m.b.H.; *J. Inst. Pet. Tech.*, 1935, **21**, 383A; *Chem. Abs.*, 1935, **29**, 6418.

[106] C. A. Getz and G. F. Smith, *Trans. Illinois State Acad. Sci.*, 1934, **27**, 71; *Brit. Chem. Abs.* **B**, 1936, 41; *Chem. Abs.*, 1935, **29**, 3414.

Chapter 30

Halogenation of Methane Homologues. Properties and Uses of Halogen Derivatives

As the number of carbon atoms in the members of the paraffin series becomes greater, the number of possible halogen-substituted derivatives increases enormously,[1] and efforts to control chlorination and thus obtain a preponderance of one halogen derivative to the exclusion of others become a matter of importance.

Hass, McBee and Weber[2] have given the following general rules for chlorination of the saturated hydrocarbons:

1. Carbon skeleton rearrangements do not occur during photochemical or thermal chlorination if pyrolysis temperatures are avoided; every possible monochloride is always formed.
2. At low temperatures the secondary and tertiary hydrogen atoms are substituted more quickly than are the primary.
3. At increasing temperatures the rates of substitution approach equality in the liquid and vapor phase.
4. Liquid phase chlorination gives relative rates of primary, secondary and tertiary substitution which are obtainable only at much higher temperatures in the vapor phase.
5. The presence or absence of moisture, carbon surfaces or light has no appreciable effect upon the rate of substitution.
6. Excessive temperatures or reaction times cause pyrolysis of the tertiary, secondary and primary chlorides in that order.
7. If a molar excess of hydrocarbon is used and the chlorinating conditions are maintained constant, the yield of monochlorides vs. polychlorides may be calculated from the equation:

$$X = KY$$

where X = weight ratio of monochlorides over polychlorides, Y = ratio of moles of hydrocarbon over moles of chlorine, and K = a constant peculiar to the hydrocarbon and the conditions.

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[1] H. P. Henze and C. M. Blair (*J.A.C.S.*, 1934, **56**, 157; *Brit. Chem. Abs.* **A**, 1934, 276; *Chem. Abs.*, 1934, **28**, 1656.) have calculated the number of disubstituted products of the paraffin series. Some of their values are as follows:

No. of Carbon Atoms	No. of Di-chlorides	No. of Carbon Atoms	No. of Di-chlorides
1	2	7	339
2	4	8	887
3	9	9	2,338
4	21	10	6,220
5	52	15	888,467
6	132	20	135,567,103

For a discussion of the number of mono-substitution products see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[2] H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, 1935, **27**, 1190; 1936, **28**, 333; *Chem. Abs.*, 1936, **30**, 78, 2913; *Brit. Chem. Abs.* **B**, 1935, 1084; **A**, 1936, 587; *J. Inst. Pet. Tech.*, 1935, **21**, 449A; 1936, **22**, 202A.

8. Dichlorination proceeds by two mechanisms: (1) loss of hydrogen chloride followed by addition of chlorine to the resulting olefin and (2) progressive substitution.

9. In vapor phase chlorination the presence of a chlorine atom on a carbon atom tends to hinder further reaction upon that carbon atom during the second substitution.

CHLORINATION OF ETHANE

In general the chlorination of ethane can be accomplished by three methods, thermal, catalytic and photochemical.[3] Temperatures from 300-500°C. are employed with 1 volume of chlorine and 8 volumes of ethane, both in the gaseous phase. If the reaction is carried out in the dark the temperature range may be limited to 360-380°C. Contact agents such as iron, thallium, alkaline-earth chlorides, charcoal and pumice impregnated with cupric chloride, which promote chlorination, are also used. Exposure to diffused daylight at 5°C., to ultraviolet rays at 80-100°C. and to the light from a mercury vapor lamp have been recommended. In the latter method ethyl chloride is not the only product; di-, tri-, tetra,- penta-, and hexachloroethane are also present, together with some ethylidine chloride.

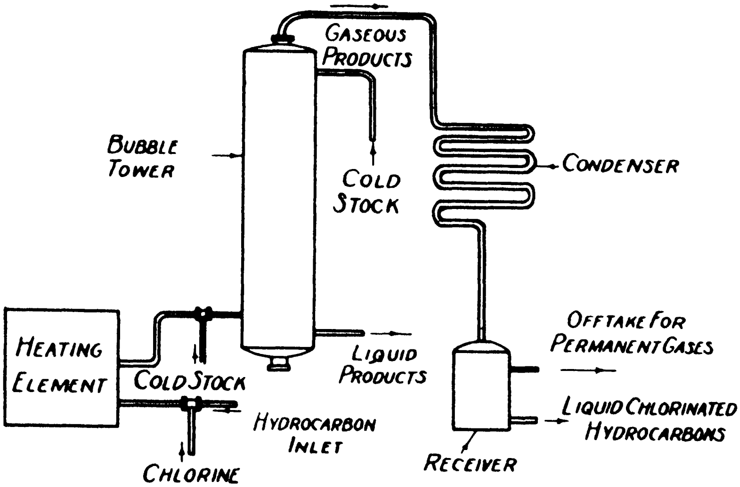

FIG. 158.—Sketch of Method for Chlorination of Gaseous Hydrocarbons. (G. Egloff)

The chlorination of still gases to secure ethyl chloride is reported by Egloff.[4] He passed a mixture of chlorine and gaseous hydrocarbons through a reaction zone which was heated to 250-750°F. The temperature of the exit gases was lowered quickly by the injection of a cooling medium consisting of some of the unreacted gases, the purpose being to prevent formation of carbon and hydrogen chloride. The products were then conducted through a bubble tower to which some fresh cold gases were added. The liquid chlorides and non-condensed materials were separated, the former being removed from the bottom of the tower. To effect chlorination in liquid phase, a solvent such as carbon tetrachloride or benzene for the above reactants has been recommended.[5]

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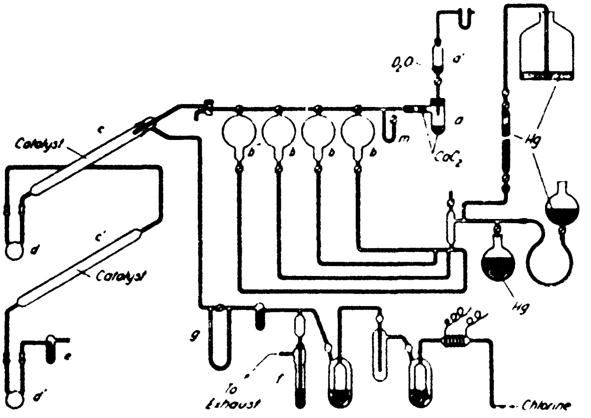
[3] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. For a review of the photochemical reactions between halogens and aliphatic hydrocarbons, see H. J. Schumacher, *Angew. Chem.*, 1936, **49**, 613; *Chem. Abs.*, 1936, **30**, 7041.

[4] G. Egloff, U. S. P. 1,950,720, March 13, 1934, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1935, 92; *Chem. Abs.*, 1934, **28**, 3576.

The preparation of alkyl polyhalides is often effected by halogenation of alkyl mono- or dichlorides. According to Hamai,[6] ethylene chloride (dichloroethane) and chlorine do not combine at 25-50°C., but if a trace of hydrogen chloride is added, trichloroethane is formed. The reaction is preceded by an induction period. To obtain hexachloroethane, Levine and Bond[7] treat perchloroethylene (C_2Cl_4) with chlorine using a contact agent of pumice impregnated with cupric chloride and excluding light.



a. Generating flask
a'. Dropping funnel
b, b', b'', b'''. Storage bulbs
c, c'. Reaction tubes
d, d'. Receivers
e. Terminal bubble counter
f Pressure regulator
g. Bubble counter
m. Manometer

Courtesy Journal of American Chemical Society

Fig. 159.—Apparatus Employed for Formation of *sym*-Dideuteriotetrachloroethane. (F. W. Breuer)

Other means of preparing ethyl chloride include the treatment of ethyl alcohol with hydrogen chloride, both in the liquid[8] and vapor[9] phases. Also, it has been suggested that gaseous ethylene be reacted with chlorine vapor to secure dichloroethane.[10] The two gases are conducted together over a promoter consisting of a mixture of zinc and stannous chlorides.

The formation of a tetrachloroethane containing two atoms of deuterium (*sym*-dideuteriotetrachloroethane) has been investigated.[11] The halogen compound was prepared by uniting heavy acetylene (dideuterioacetylene) with chlorine. The apparatus consisted of an acetylene-generating flask, a storage system of four bulbs to hold the acetylene, and two reaction chambers of heavy-walled tubing joined to receiving flasks (see Fig. 159). A chlorine-purifying train was connected to the reaction chamber at the same point that the heavy acetylene entered. The rate of acetylene was maintained constant by employing mercury as a confining liquid in the storage flasks. In the procedure a catalyst consisting of ferric oxide, reduced iron, aluminum oxide, powdered antimony and sand was employed. The heavy acetylene was generated by allowing deuterium oxide (heavy water) to fall upon calcium carbide. The chlorination was then effected by conducting chlorine at the rate of 16 cc. per minute and acetylene at 4 cc. per minute into the reaction chamber. The latter was heated by a 100 watt incandescent lamp at a distance of 40 cm. A yield of 78 per cent of the theoretical amount of *sym*-dideuteriotetrachloroethane was reported to be obtained.

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[5] French P. 773,679, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1430.

[6] S. Hamai, *Bull. Chem. Soc. Japan*, 1934, **9**, 542; *Brit. Chem. Abs.* **A**, 1935, 325; *Chem. Abs.*, 1935, **29**, 1771.

[7] A. A. Levine and H. A. Bond, U. S. P. 2,037,419, April 14, 1936, to E. I. du Pont de Nemours and Co.; *Chem. Abs.*, 1936, **30**, 3837.

[8] E. Teupel, U. S. P. 1,950,827, March 13, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 3424. German P. 594,551, 1934; *Chem. Abs.*, 1934, **28**, 4434. French P. 793,731, 1936; *Chem. Abs.*, 1936, **30**, 4514.

[9] P. Ernst, U. S. P. 1,937,269, Nov. 28, 1933, to A. Wacker Ges. für elektrochemische Industrie; *Chem. Abs.*, 1934, **28**, 1052; *Brit. Chem. Abs.* **B**, 1934, 824.

[10] British P. 448,269, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 7127. French P. 793,744, 1936; *Chem. Abs.*, 1936, **30**, 4515. For the reactions of olefins with halogens, see Chapter 20.

[11] F. W. Breuer, *J.A.C.S.*, 1936, **58**, 1289; *Chem. Abs.*, 1936, **30**, 5936.

The properties of this "heavy" tetrachloroethane were compared with those of the compound containing ordinary hydrogen. Some of these properties are indicated in Table 155.

TABLE 155.—*Physical Properties of Tetrachloroethanes.*

	sym-Dideuteriotetrachloroethane $CDCl_2CDCl_2$	*sym*-Tetrachloroethane $CHCl_2CHCl_2$
B.p. (737 mm.) ..	145.7° ± 0.05°C.	145.2° ± 0.05°C.
d_4^{20}	1.6118	1.5943
n_D^{20}	1.4924	1.4940

PROPERTIES OF CHLORINATED ETHANE

The work of van der Lee[12] indicates that over the range 62.1 to 239.1°C. the vapor pressure of hexachloroethane is inversely proportional to the temperature and may be represented by the equations:

$$\log_{10} p = \frac{-2636.1}{T} + 8.640 \text{ for the liquid and}$$

$$\log_{10} p = \frac{-2103.6}{T} + 7.483 \text{ for the solid}$$

where p = vapor pressure and T = absolute temperature. The same investigator found the triple point[13] to be 186.8°C. and calculated the heats of sublimation, vaporization and fusion as 12.0, 9.6 and 2.4 kilogram calories per mole, respectively. The same figure for the triple point was obtained by Wiebenga.[14]

To stabilize tetrachloroethane and to prevent development of an objectionable degree of acidity a number of agents have been suggested. They include phenolic substances[15] (hydroquinone, p-cresol, resorcinol), propanol,[16] a mixture of a free fatty acid and soap,[17] butyl oxide,[18] and small proportions (0.05 per cent) of caffeine.[19] To determine the applicability of stabilizers, Dietrich and Lohrengel[20] treat the chlorinated hydrocarbon (both with and without incorporation of stabilizers) with oxygen at 25 atmospheres and 100°C. for 4 hours in the presence of water. The quantity of hydrogen chloride liberated is afterwards ascertained. Water prevents the formation of any appreciable proportion of phosgene by hydration of the chloride.

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[12] P. J. van der Lee, *Z. anorg. allgem. Chem.*, 1935, **223**, 213; *Brit. Chem. Abs.* **A**, 1935, 1064; *Chem. Abs.*, 1935, **29**, 6118. The toxicity of a number of chlorohydrocarbons is discussed by K. B. Lehman and L. Schmidt-Kehl, *Arch. Hyg. Bakt.*, 1936, **116**, 131; *Chem. Abs.*, 1937, **31**, 477.

[13] The triple point is the temperature at which the solid, liquid and vapor phases of a substance are in equilibrium.

[14] E. H. Wiebenga, *Z. anorg. allgem. Chem.*, 1935, **225**, 38; *Brit. Chem. Abs.* **A**, 1936, 20; *Chem. Abs.*, 1936, **30**, 672.

[15] P. J. Carlisle and C. R. Harris, Canadian P. 341,792, 1934, to Canadian Industries Ltd.; *Chem. Abs.*, 1934, **28**, 5076. *Cf.* British P. 397,915, 1933, to Roessler and Hasslacher Chemical Co.; *Chem. Abs.*, 1934, **28**, 1046; *Brit. Chem. Abs.* **B**, 1933, 956.

[16] French P. 794,653, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 5235.

[17] J. Savage and A. V. Pitter, Canadian P. 343,936, 1934, to Canadian Industries Ltd.; *Chem. Abs.*, 1934, **28**, 7260.

[18] J. M. G. de Schacken and M. E. A. Schmidt, French P. 794,878, 1936; *Chem. Abs.*, 1936, **30**, 5430.

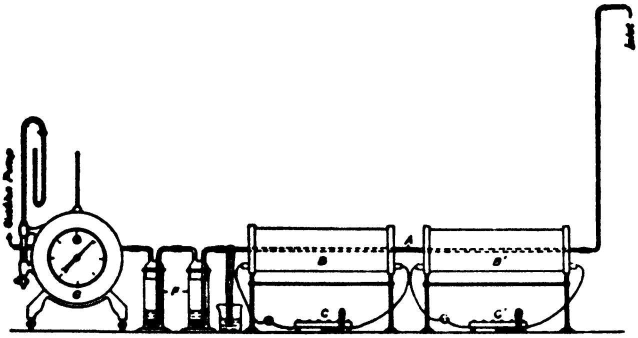
[19] P. J. Carlisle, Canadian P. 353,451, 1935, to Canadian Industries Ltd.; *Chem. Abs.*, 1935, **29**, 7999.

[20] K. R. Dietrich and W. Lohrengel, *Angew. Chem.*, 1934, **47**, 830; *Chem. Abs.*, 1935, **29**, 2505; *Brit. Chem. Abs.* **B**, 1935, 137.

A proposed method for the quantitative determination of gaseous dichloroethane and ethyl chloride has been reported.[21] It is based upon the oxidation of the halides to form carbon dioxide, water and chlorine.

$$C_2H_4Cl_2 + 3O_2 \longrightarrow 2CO_2 + 2H_2O + Cl_2$$

The latter may then be absorbed in an appropriate reagent. The apparatus consisted of two electrically heated furnaces containing a quartz tube which was connected at one end to the incoming vapors and at the other to absorption bottles (see Fig. 160). A gas meter was employed to measure the rate of flow, which was controlled by a suction pump. The absorption bottles contained sodium arsenate to remove the chlorine. The gases under investigation were drawn through the combustion furnaces at the rate of 20 liters per hour. During the period of contact the furnace was maintained at temperatures in the range 900-950°C. When the combustion was completed, the apparatus was blown with air to remove all chlorine, and the amount of the latter held in the absorption liquid was determined. It was stated that the estimation of dichloroethane was accurate within 0.04 per cent by volume. However, it was said that the ethyl chloride determinations had an accuracy of ±10 per cent if 2 per cent or more of ethyl chloride was present.



A. Quartz tube
B, B'. Electric furnaces
C, C'. Resistance units
F. Absorption bottles
G. Gas meter

Courtesy Industrial and Engineering Chemistry

FIG. 160.—Apparatus for Combustion Method of Determining Gaseous Chlorinated Hydrocarbons. (M. J. Martinek and W. C. Marti)

USES OF CHLORINATED ETHANES

The chlorides of ethane have many varied applications, being employed in the preparation and purification of organic compounds, in refining and dewaxing lubricating oils, as refrigerants, in the manufacture of insecticidal compositions and as dry cleaning agents.[22]

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[21] M. I. Dement'eva and E. K. Serebryakova, *Materials on Cracking and Chemical Treatment of Products Obtained, Khimteoret (Leningrad)*, 1935, No. 2, 146; *Chem. Abs.*, 1935, 29, 6033; *Brit. Chem. Abs.* B, 1936, 625. The apparatus employed is described by M. J. Martinek and W. C. Marti, *Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 408; *Chem. Abs.*, 1931, 25, 5875.

Monochloroethane. To secure ethylated cellulose, Nikitin and Rudneva[23] recommend cellulose and ethyl chloride. They report that a temperature of 100-120°C. causes complete reaction in 5 hours and that a large excess of concentrated sodium hydroxide favors the production of a highly ethylated compound. The suggestion has been made that this chloroethane be used in a refrigerant mixture. For this purpose methylene chloride and monochloroethane are said to possess the advantage, according to Davenport,[24] that at room temperature (20°C.) they have a vapor pressure of less than 1 atmosphere. The two latter halides are also used as solvents for insecticidal compositions.[25]

Dichloroethane. Reilly[26] reports that when chlorine (containing 20 per cent of air) and dichloroethane are separately preheated to 120-180°C. and passed over coke at 375°C. they yield tetrachloroethylene. Dichloroethane may be employed as a solvent for crude naphthalene when the latter is refined with sulphuric acid[27] and as an extractant for sulphur in gas-purification residues.[28] Ethylidene chloride mixed with kerosene or benzene may be used as a dehydrating agent for aliphatic acids, such as acetic, and for the acid-anhydride product of thermal decomposition of these acids.[29] Ethylene chloride, alone[30] or incorporated with benzene,[31] isopropyl ether or amyl alcohol,[32] is a dewaxing agent for lubricating oils. In one dry cleaning process, a mixture of 75 per cent of dichloroethane and 25 per cent of trichloroethylene may be employed.[33] MacLang[34] effects selective extraction of caffeine with dichloroethane. The coffee is heated with water until a 16 per cent moisture content is attained, then the pressure is raised to 5 atmospheres and the temperature to 125°C. At the end of 30 minutes preheated dichloroethane is introduced and extraction brought about. The caffeine content of the coffee is lowered to 0.08 per cent by this means. It is also interesting to note that when incorporated with paraffin wax and resin the halide is reported to furnish a scouring agent for painted and waxed surfaces.[35]

[22] The narcotic effect of chlorinated derivatives of ethane has been studied by P. Schwander, *Arch. Gewerbepath. Gewerbehyg.*, 1936, 7, 109; *Brit. Chem. Abs.* **A** (3), 1937, 64.

[23] N. I. Nikitin and T. I. Rudneva, *J. Appl. Chem. (U.S.S.R.)*, 1933, **6**, 45; *Chem. Abs.*, 1933, **27**, 5964; *Brit. Chem. Abs.* **A**, 1933, 812.

[24] R. H. Davenport, U. S. P. 1,986,959, Jan. 8, 1935, to Chicago Pneumatic Tool Co.; *Chem. Abs.*, 1935, **29**, 1294; *Brit. Chem. Abs.* **B**, 1935, 1074.

[25] L. Hess, German P. 587,747, 1933, to J. D. Riedel-E. de Haën A.-G.; *Chem. Abs.*, 1934, **28**, 1810.

[26] J. H. Reilly, U. S. P. 1,947,491, Feb. 20, 1934, to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1934, 1094. For the purification of tetrachloroethylene see G. H. Coleman, U. S. P. 2,000,881, May 7, 1935, to Dow Chemical Co.; *Chem. Abs.*, 1935, **29**, 4029.

[27] K. Fujiki and G. Royama, Japanese P. 100,609, 1933, to The Head of the Tokyo Kogyo Shikenjo; *Chem. Abs.*, 1934, **28**, 3427. Extraction of oils and fats with dichloroethane is reported by M. Pourbaix, *15me Congr. chim. ind.* (*Bruxelles*, Sept., 1935), **1936**, 567; *Chem. Abs.*, 1936, **30**, 5822.

[28] British P. 430,110, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1935, 948; *Chem. Abs.*, 1935, **29**, 8257.

[29] H. Dreyfus, British P. 403,075, 1933; *Chem. Abs.*, 1934, **28**, 2729; *Brit. Chem. Abs.* **B**, 1934, 312.

[30] A. I. Voronov, N. I. Logvinova, *Neft. Khoz.*, 1934, **26** (4), 57; *Chem. Abs.*, 1934, **28**, 7507. French P. 790,852, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 3223. P. Astrakhantzev, *Masloboino Zhirovoe Delo.*, 1933, **9** (8), 10; *Chem. Abs.*, 1935, **29**, 3183.

[31] L. D. Jones, British P. 447,415, 1936, to Sharples Specialty Co.; *Brit. Chem. Abs.* **B**, 1936, 916; *Chem. Abs.*, 1936, **30**, 7326.

[32] B. Y. McCarty and W. E. Skelton, U. S. P. 1,988,397 and 1,988,398, April 16, 1935, to Texas Co.; *Chem. Abs.*, 1935, **29**, 3822; *J. Inst. Pet. Tech.*, 1935, **21**, 221A.

[33] French P. 785,864, 1935, to Compagnie des produits chimiques et electrometallurgiques Alais, Froges et Camargue; *Chem Abs.*, 1936, **30**, 629. The use of chlorinated solvents in dry cleaning is discussed by D. H. Killeffer, *Ind. Eng. Chem.*, 1936, **28**, 640; *Chem. Abs.*, 1936, **30**, 4678; *Brit. Chem. Abs.* **B**, 1936, 787. See also R. G. Harry, *Paint Manuf.*, 1936 **6**, 288; *J. Inst. Pet. Tech.*, 1936, **22**, 514A; *Chem. Abs.*, 1936, **30**, 7718.

[34] J. MacLang, U. S. P. 2,023,333, Dec. 3, 1935, to Coffex A.-G.; *Chem. Abs.*, 1936, **30**, 784.

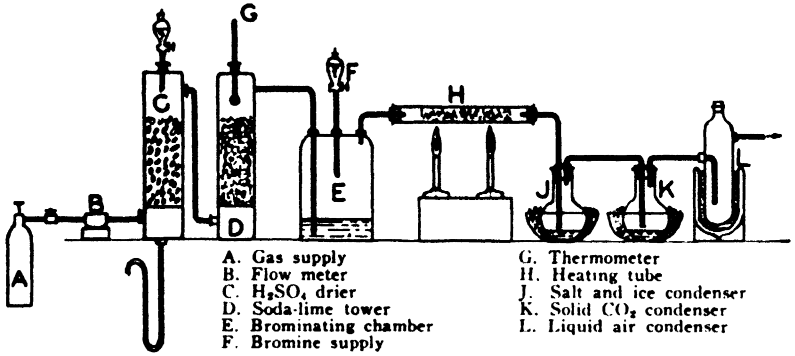
[35] A. Abraham and M. L. A. Philippon, British P. 440.525, 1935; *Brit. Chem. Abs.* **B**, 1936. 285; *Chem. Abs.*, **1936**, **30**, 3912.

Higher Chloroethanes. *unsym*-Tetrachloroethane reacts with concentrated sulphuric acid, at 100-160°C., to give monochloroacetic acid.[36]

Anhydrous tetrachloroethane may be employed as cooling medium for cold storage. To prevent evaporation of the halide, the latter is covered with a layer of glycerol or glycol, and to inhibit formation of corrosive acid, calcium, sodium or lead oxide is incorporated.[37]

Starr and Beiswenger[38] point out that a solvent mixture composed of phenol and tetrachloro derivatives is applicable for processing mineral oils.

In one method for the manufacture of motion picture films, cellulose acetate is dissolved in dichloroethylene and propyl alcohol, to which is added tetrachloroethane. The function of the latter, which has a higher boiling point than the olefin chloride, is to improve the mechanical properties of the resulting film.[39]



A. Gas supply
B. Flow meter
C. H_2SO_4 drier
D. Soda-lime tower
E. Brominating chamber
F. Bromine supply
G. Thermometer
H. Heating tube
J. Salt and ice condenser
K. Solid CO_2 condenser
L. Liquid air condenser

Courtesy Industrial and Engineering Chemistry

FIG. 161.—Method for Bromination of Saturated Gaseous Hydrocarbons. (W. J. Perelis)

Sullivan[40] suggested a combination of carbon tetrachloride, tetrachloroethane, naphtha and a small amount (0.1-2 per cent) of a chlorinated derivative of naphthalene as a dry cleaning fluid. Grebe and Mills[41] recommended tetrachloromethane and tetrachloroethane for the same purpose. This latter composition was reported to be noninflammable and nonexplosive and to evaporate from the articles cleaned in less than 5 minutes. Lindner[42] uses gasoline and tetrachloroethane as a dry cleaning agent. Reddish[42a] points out that the addition of water to chlorinated hydrocarbons used in dry cleaning will effect the removal of water-soluble soil and oil-soluble soil in one operation. To overcome the possibility of "water-spotting" the fabrics during cleaning, he suggests an "absorbefacient"[42b] to maintain the moisture present in a dispersed state. One such "absorbefacient" consists of 25 per cent oleic acid, 25 per cent naphtha and 50 per cent mahogany sodium sul-

[36] French P. 774,172, 1934, to Compagnie des produits chimiques et électrométallurgiques Alais, Froges et Camargue; *Chem. Abs.*, 1935, **29**, 2179.

[37] British P. 409,844, 1934, to Platen-Munters Refrigerating System Aktiebolag (to Electrolux Ltd.); *Chem. Abs.*, 1934, **28**, 6217.

[38] J. V. Starr and G. A. Beiswenger, Canadian P. 356,174, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 2745.

[39] British P. 421,768, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1935, 266; *Chem. Abs.*, 1935, **29**, 3836.

[40] F. W. Sullivan, Jr., U. S. P. 2,017,327, Oct. 15, 1935, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 8362.

[41] J. J. Grebe and L. E. Mills, U. S. P. 1,989,478, Jan. 29, 1935, to Dow Chemical Co.; *Chem. Abs.*, 1935, **29**, 2000.

[42] D. Lindner, Hungarian P. 112,897, 1935; *Chem. Abs.*, 1935, **29**, 8187.

[42a] W. T. Reddish, U. S. P. 2,061,211, Nov. 17, 1936, to Emery Industries, Inc.; *Chem. Abs.*, 1937, **31**, 888.

[42b] An "absorbefacient" is a composition which dissolves in a cleaning solvent and which, though it does not readily absorb any substantial amount of moisture, renders the cleaning solvent capable of absorbing moisture.

phonate.[42c] In the cleaning operation a concentration of 6 per cent of the above compound is employed, together with a quantity of moisture equal to 5-15 per cent of the weight of the garments to be cleaned.

According to Balázs an atmosphere containing tetrachloroethane and trichloroethylene in the ratio 4:1 is very effective as an insecticide.[43] Another agent consists of finely powdered derris root, solid hexachloroethane and chalk.[44] Yamazaki[45] prefers a mixture of borax, hexachloroethane and a hydrofluoric acid solution of glass for the same purpose.

BROMINATION OF ETHANE

Merz and Weith[46] predicted, from experiments on the bromination of ethyl iodide, that the bromination of ethane would lead to tetrabromo- and hexabromoethane. Perelis,[47] on the other hand, reports that at a sufficiently low halogen concentration, mixtures of ethane and bromine (using an iron catalyst) lead mainly to the formation of monohalides, when the reaction temperature is maintained at 350°C. In effecting such an operation gaseous ethane was bubbled through a layer of liquid bromine, and the resulting mixture conducted through the heated reaction zone. To maintain a constant depth of liquid, fresh bromine was added intermittently throughout the reaction. Some of his results are shown in Table 156.

TABLE 156.—*Bromination of Ethane at 350°C.*

Bromine Layer Mm.	Conversion per Passage %	Analysis of Products Mono-Bromides Mole %	Dibromides Mole %
9.5	——	81.2	18.8
8.5	10.0	88.3	11.7
8.5	6.89	88.89	11.11
9.5	——	92.94	7.06
11.5	14.7	94.88	5.12
16.5	13.58	91.7	8.3
22.5	15.03	92.3	7.7
22	21.2	89.1	10.9
22	23.2	85.59	14.41
22	23.61	84.5	15.5

FLUORINATION OF ETHANE

Direct fluorination of methane homologues has not been reported. However, the preparation of fluoro-halo derivatives has received attention. For example, hydrogen fluoride will unite with dichloroethane when a catalyst such as ferric chloride and activated carbon is used.[48] Other contact agents include a halide of copper, silver, gold, zinc, cadmium, mercury, vanadium, manganese, cobalt, nickel or platinum dispersed in carbon which serves as a carrier.[49] Daudt and Youker[50] combined antimony pentachloride with hydrogen fluoride and added trichloroethane to yield monofluorodichloroethane. The presence of a liquid medium which is not reacted upon by fluorine, such as anhydrous hydrogen fluoride at —40°C., is recommended for the substitution of fluorine in tetrachloroethane.[51] Henne[52] prepared trichlorotrifluoroethane by reacting antimony trichloride with hexachloroethane and then treating the resulting compound with fluorine or hydrogen fluoride. The same investigator[53] points out that antimony trifluoride and chlorine may be employed in a similar method.

[42c] The mahogany sulphonates are discussed in Chapter 46.

[43] A. Balázs, French P. 787,963, 1935; *Chem. Abs.*, 1936, **30**, 1504. British P. 453,364, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 516A; *Chem. Abs.*, 1937, **31**, 1152; *Brit. Chem. Abs.* **B**, 1936, 1182.

[44] British P. 410,364, 1934, to Aktiengesellschaft für medizinische Produkte; *Chem. Abs.*, 1934, **28**, 6260; *Brit. Chem. Abs.* **B**, 1934, 734.

[45] B. Yamazaki, Japanese P. 111,065, 1935, to K. K. Umeda Kimò Senshoku Kôjò; *Chem. Abs.*, 1936, **30**, 2407.

[46] V. Merz and W. Weith, *Ber.*, 1878, 11, 2235; *J.C.S.*, 1879, **36**, 302.

[47] W. J. Perelis, *Ind. Eng. Chem.*, 1933, **25**, 1160; *Brit. Chem. Abs.* **A**, 1933, 1271; *Chem. Abs.*, 1933, **27**, 5713.

[48] British P. 428,445, 1935, to Kinetic Chemicals, Inc.; *J. Inst. Pet. Tech.*, 1935, **21**, 313A; *Chem. Abs.*, 1935, **29**, 6901. Canadian P. 349,160, 1935; *Chem. Abs.*, 1935, **29**, 3685.

[49] British P. 428,361, 1935, to Kinetic Chemicals, Inc.; *J. Inst. Pet. Tech.*, 1935, **21**, 269A; *Chem. Abs.*, 1935, **29**, 6605; *Brit. Chem. Abs.* **B**, 1935, 664.

[50] H. W. Daudt and M. A. Youker, Canadian P. 349,159, 1935, to E. I. du Pont de Nemours & Co., to Kinetic Chemicals, Inc.; *Chem. Abs.*, 1935, **29**, 3685.

Also, it has been suggested that mercuric fluoride be employed to effect the substitution of fluorine in an alkyl halide.[54] Thus, the preparation of ethyl fluoride from ethyl bromide and mercuric fluoride was reported. The apparatus consisted of a copper reaction vessel equipped with a copper reflux condenser. The latter was kept at 0°C. throughout the reaction. Ethyl bromide was placed in the vessel and mercuric fluoride slowly added. During the incorporation of the mercuric salt, the reaction vessel was immersed in an ice bath. It was stated that ethyl fluoride is generated as soon as the reagents come in contact. This halide passes through the reflux condenser and may be collected in a receiver cooled with solid carbon dioxide, while ethyl bromide is returned by the condenser to the reaction chamber. The yield of ethyl fluoride was said to be quantitative, all the salt left in the reaction vessel being mercuric bromide.

Properties of Fluorinated Ethane. The work of Henne and Midgley[55] indicates that the monofluoride and 1,2-difluoride of ethane are relatively unstable, readily undergoing hydrolysis and further fluorination. However, as soon as two fluorine atoms are attached to one carbon, the compound becomes stable and can be fluorinated further with difficulty. This effect is noticeable not only on the atom to which the fluorine is bound, but also upon the adjacent carbon.

TABLE 157.—*Properties of Fluorohaloethanes.*

Compound	M.P. °C.	B.P. °C.	T°C.	d_4	n_α	n_D	n_β
$CHCl_2CCl_2F$	− 82.6	116.6	20.0	1.62232	1.44634	1.44873	1.45873
$CHClFCCl_3$	− 95.35	117.0	20 0	1.62525	1 45005	1.45253	1.45861
$CHCl_2CClF_2$		71.9	25 0	1.5447		1 3889	
$CHClFCCl_2F$	Glass	72.5	20.0	1.55868	1.39216	1.39419	1.39873
CHF_2CCl_3	Glass	73.0	20.0	1.56613	1.39590	1.39787	1 40278
$CHClFCF_2Cl$		28.0	10.0	1.496			
CHF_2CF_2Cl		− 12					
CH_3CCl_2F		31.7	5.0	1.2673		1 38679	
$CH_2ClCHClF$		73.7	20.0	1.3814		1 41132	
CH_2ClCHF_2		35.1	15.0	1.312		1.3528	
$CH_2BrCHClF$		96 6	20.0	1.82913		1.45463	
CH_2BrCH_2F		71.5	25.0	1.7044		1.42261	
$CHClBrCHClF$		124.7	20.0	1.932		1.4776	
$CHClBrCHF_2$		82.3	20.0	1.879		1.4173	

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[51] W. S. Calcott and A. F. Benning U. S. P. 2,013,030, Sept. 3, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 6900.

[52] A. L. Henne, U. S. P. 2,013,050, Sept. 3, 1935, to General Motors Corp.; *Chem. Abs.*, 1935, **29**, 6900; *Brit. Chem. Abs.* **B**, 1936, 919. *Cf.* U. S. P. 2,007,198, July 9, 1935; *Chem. Abs.*, 1935, **29**, 5459. U. S. P. 1,970,562, August 21, 1934; *Brit. Chem. Abs.* **B**, 1935, 715; *Chem. Abs.*, 1934, **28**, 6159. British P. 378,324, 1932; *Chem. Abs.*, 1933, **27**, 3947; *Brit. Chem. Abs.* **B**, 1932, 1019. German P. 594,751, 1934, to Frigidaire Corp.; *Chem. Abs.*, 1934, **28**, 4430.

[53] A. L. Henne, U. S. P. 1,987,840, Oct. 30, 1934, to General Motors Corp.; *Brit. Chem. Abs.* **B**, 1935, 839; *Chem. Abs.*, 1935, **29**, 175. *Cf.* French P. 798,421, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 7121.

[54] A. L. Henne and T. Midgley, Jr., *J.A.C.S.*, 1936, **58**, 884; *Chem. Abs.*, 1936, **30**, 5176; *Brit. Chem. Abs.* **A**, 1936, 961.

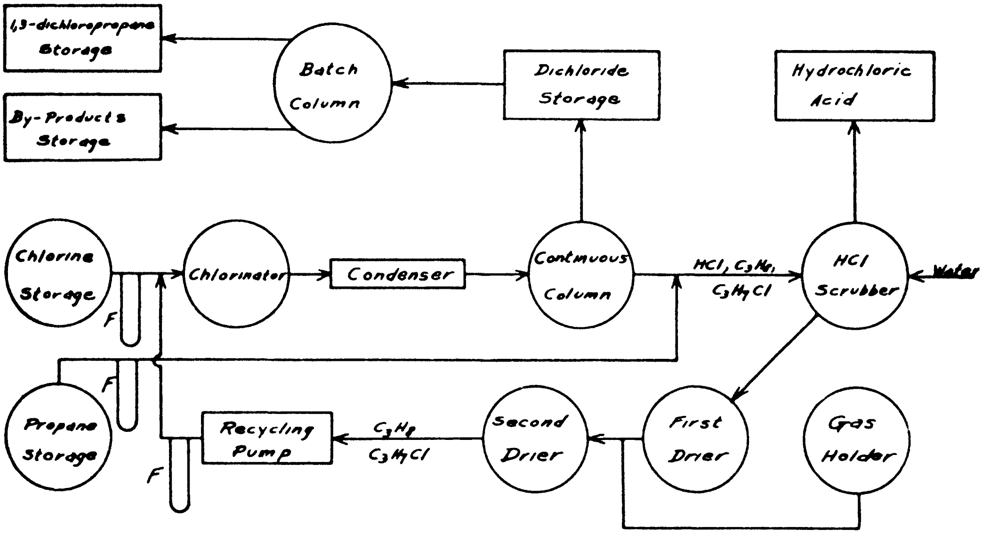
[55] A. L. Henne and T. Midgley, Jr., *J.A.C.S.*, 1936, **58**, 982; *Chem. Abs.*, 1936, **30**, 5175; *Brit. Chem. Abs.* **A**, 1936, 961.

The melting points, boiling points, densities and indices of refraction (for the red, yellow and blue lines, respectively) of some fluorohaloethanes have been compiled by Henne and his coworkers.[56] They are listed in Table 157.

THE CHLORINATION OF PROPANE

The chlorination of propane has been achieved by two general methods, (1) thermal treatment in the absence of light and oxygen and (2) in the presence of catalysts.

Chlorine and propane may be separately preheated to 100°C. and mixed in enameled metal or Pyrex glass chambers, without exposure to light. The product of the reaction is propyl chloride.[57] The process may be varied by passing a stream of chlorine into a current of the hydrocarbon at the above temperature.[58] To avoid explosion, the propane is present in excess and the speed of the chlorine is greater than the critical velocity at which ignition would occur.[59] Britton, Coleman and Hadler[60] report that during chlorination of propane some hydrogen chloride and propene are formed. However, by raising the temperature to 195-199°C. these two can be combined to give the saturated halide.



Courtesy Industrial and Engineering Chemistry

FIG. 161A.—Flow Diagram for Chlorination of Propane. (H. B. Hass, E. T. McBee, G. E. Hinds and E. W. Gluesenkamp)

Deanesly[61] has made a study of certain of the factors which influence the halogenation of propane. He states that oxygen inhibits the reaction, whether the latter be catalyzed by light or by olefins simultaneously reacting. This effect is utilized in one process in which addition, rather than substitution, is desired. Thus, a mixture of unsaturated and paraffin hydrocarbons is treated with a halogen and oxygen to give olefin halides.[62] According to the above investigator[63] chlorination of propane can be brought about by adding free chlorine in the dark, in the absence of oxygen, and below 100°C. A small amount of an olefin (propene) in the reaction chamber is reported to increase the speed of substitution. The chlorination of a mixture of propane and 1-monochloropropane has been utilized to prepare 1,3-dichloropropane.[63a] In the procedure an excess (10:1) of the hydrocarbon and monohalide over chlorine was maintained to inhibit the formation of trichloro derivatives. The chlorine was allowed to react completely, so that the product flowing to the condenser and rectifying column (Fig. 161A) consisted of 1- and 2-monochloropropane, 1,1-, 1,3-, 1,2-, and 2,2-dichloropropanes, as well as hydrogen chloride. Because of the widely separated boiling points of these substances (Fig. 161B), removal of a relatively pure 1,3- derivative at 120.4°C. was said to be effectively accomplished. The latter compound was employed in the synthesis of cyclopropane, used as an anesthetic.[63b]

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[56] A. L. Henne and E. C. Ladd. *J.A.C.S.*, 1936, 58, 402; *Chem. Abs.*, 1936, **30**, 2914; *Brit. Chem. Abs.* **A**, 1936, 703. A. L. Henne and M. W. Renoll. *J.A.C.S.*, 1936, **58**, 887; *Brit. Chem. Abs.* **A**, 1936, 961; *Chem. Abs.*, 1936 **30**. 5175.

[57] German P. 608,360, 1935, to Bataafsche Petroleum Maatschappij; *J. Inst. Pet. Tech.*, 1935, **21**, 224A; *Chem. Abs.*, 1935, **29**, 2549.

[58] German P. 610,660, 1935, to Sharples Solvents Corp.; *Chem. Abs.*, 1935, **29**, 5855.

[59] German P. 607,461, 1934, to Sharples Solvents Corp.; *J. Inst. Pet. Tech.*, 1935, **21**, 269A.

[60] E. C. Britton, G. H. Coleman and [illegible] C. Hadler, U. S. P. 2,018,345, Oct. 22, 1935, to Dow Chemical Co.; *Chem. Abs.*, 1936, **30**, 106; *Brit. Chem. Abs.* **B**, 1936, 1192.

[61] R. M. Deanesly, *J.A.C.S.*, 1934, **56**, 2501; *Chem. Abs.*, 1935, **29**, 724; *Brit. Chem. Abs.* **A**, 1935, 62.

The catalytic chlorination of di- and tri-chloropropanes has received attention,[64] but relatively few reports on direct halogenation of the hydrocarbon (propane) by the aid of contact agents have been noted. Sharp[65] points out that cupric or ferric chloride will aid the chlorination of propane if mono- and dichloropropane are also present. The use of actinic rays and of successive reaction stages at progressively higher temperatures is recommended in this procedure.

In the monochloride fraction which Schorlemmer[66] obtained by the photochemical chlorination of propane, he reported only 1-chloropropane. Later work by Hass, McBee and Weber[67] indicates that with the use of more modern rectification equipment a yield of 60 per cent 2-chloropropane and 40 per cent 1-chloropropane can be obtained.

Yuster and Reyerson[68] show that the homogeneous (single phase) chlorination of propane is of the chain type, as evidenced by an induction period, the inhibitory effect of oxygen and the fact that a packed chamber reduces the extent of halide formation. They conclude that the complete picture is extremely complicated and is an eight-stage process with an enormous number of combinations in the intermediate stages. High partial pressures of propane eliminate explosions and favor the production of monochloropropane (75 per cent), with a conversion of 90 per cent of the chlorine input.

The heterogeneous reaction in the presence of aluminum oxide, copper and cupric chloride deposited on a silicon dioxide gel is described by the same investigators.[69] The extent of chlorination increases with a rise of temperature, but when complete conversion is attained, the temperature can be reduced without diminishing the yield of halides. High partial pressure of chlorine, rising temperatures and greater rates of flow lead to di- and trichloropropanes, but tend to render the catalyst inactive. The view that secondary chlorination of the propene (arising from the pyrolysis of propyl chloride) takes place is supported by the fact that a large proportion of 1,2-dichloropropane is obtained.

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[62] British P. 402,928, 1933, to Bataafsche Petroleum Maatschappij; *J. Inst. Pet. Tech.*, 1934, **20**, 115A; *Brit. Chem. Abs.* **B**, 1934, 266.

[63] R. M. Deanesly, U. S. P. 1,991,600, Feb. 19, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 2174. Canadian P. 338,210, 1933; *Chem. Abs.*, 1934, **28**, 1714.

[63a] H. B. Hass, E. T. McBee, G. E. Hinds and E. W. Gluesenkamp, *Ind. Eng. Chem.*, 1936, **28**, 1178; *J. Inst. Pet. Tech.*, 1936, **22**, 551A; *Brit. Chem. Abs.* **B**, 1936, 1140.

[63b] See Chapter 53, this text.

[64] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[65] W. E. Sharp, U. S. P. 2,010,039, Aug. 6, 1935; *Chem. Abs.*, 1935, **29**, 6252.

[66] C. Schorlemmer, *Proc. Roy. Soc. (London)*, 1868, 17, 372; *Ann.*, 1869, 150, 210; *Ann. Chim. Phys.*, 1870, 19 (4), 439.

[67] H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, 1935, **27**, 1190; *J. Inst. Pet. Tech.*, 1935, **21**, 449A; *Chem. Abs.*, 1936, **30**, 78; *Brit. Chem. Abs.* **B**, 1935, 1084.

[68] S. Yuster and L. H. Reyerson, *J. Phys. Chem.*, 1935, **39**, 859; *J. Inst. Pet. Tech.*, 1935, **21**, 335A; *Chem. Abs.*, 1935, **29**, 6822; *Brit. Chem. Abs.* **A**, 1935, 1082.

[69] L. H. Reyerson and S. Yuster, *J. Phys. Chem.*, 1935, **39**, 1111; *Brit. Chem. Abs.* **A**, 1936, 35; *Chem. Abs.*, 1936, **30**, 429.

Uses of Chlorinated Propane. Propene chloride is used with methyl or ethyl alcohol in the preparation of lacquers containing cellulose acetate.[70] 1,2-Dichloropropane and methanol are not individual solvents for cellulose acetate, but solvent action is obtained when a composite of the two containing 70 per cent of the halide and 30 per cent of the alcohol is employed. When mixed with carbon tetrachloride, the former is reported to be superior to carbon disulphide as a fumigant.[71] Also, 1,2-dichloropropane has been employed together with dichloropropene in dewaxing oils.[71a] As a dry cleaning agent, trichloropropane has been suggested.[72] One of the reported advantages of this substance is its relatively low toxicity and the fact that it is non-flammable.

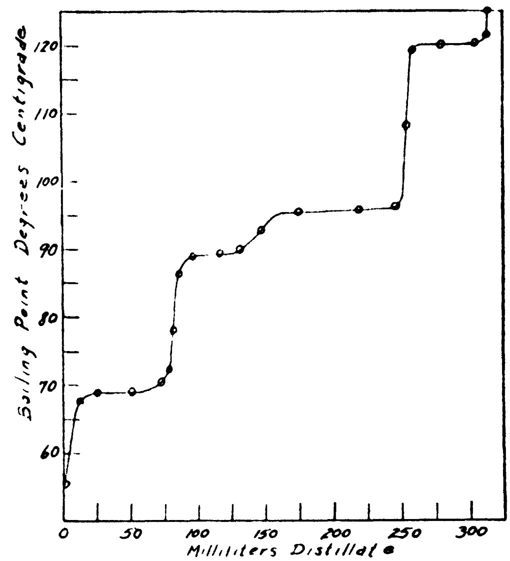

FIG. 161B.
Rectification Curve for Dichloropropanes (H. B. Hass, E. T. McBee, G. E. Hinds and E. W. Gluesenkamp)

Courtesy Industrial and Engineering Chemistry

CHLORINATION OF BUTANE

According to Deanesly[72a] the formation of mono- and dichlorobutanes from chlorine and butane in the absence of light is induced if butene is simultaneously introduced into the reaction zone. Oxygen is excluded and the temperature range may be extended from —41° to 100°C. Clark[72b] points out that butane may be halogenated in the vapor phase by admixing the hydrocarbon and chlorine. The products are led to a fractionating column where the halogenated derivatives are separated. Hydrogen chloride and unreacted butane may then be recycled to act as a reflux. For a continuous-flow process involving vapor phase operations and acceleration by actinic light, isobutane and chlorine are conducted at 250°C. through a reaction chamber, the walls of this chamber being maintained at 200°C. The vapors are kept in contact for a period of 10 seconds and the products rapidly cooled at 100°C. at the end of that time. In this manner the production of olefins and chloroölefins is said to be prevented.[72c]

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[70] E. W. Reid. U. S. P. 1,969,183. Aug. 7, 1934, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1934, **28**, 6328; *Brit. Chem. Abs.* **B**, 1935. 599.

[71] J. A. Munro and A. C. Fox. *N. Dakota Agric. Exp. Sta. Bull.*, 1934, **278**; *Brit. Chem. Abs.* **B**, 1936, 38; *Chem. Abs.*, 1935, **29**, 5586.

[71a] British P. 454,176, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1937, **31**, 1603; *Brit. Chem. Abs.* **B**, 1936, 1139; *J. Inst. Pet. Tech.*, 1936, **22**, 548A.

[72] W. E. Sharp, U. S. P. 2,010,038, Aug. 6, 1935; *Brit. Chem. Abs.* **B**, 1936, 930; *Chem. Abs.*, 1935, **29**, 6440.

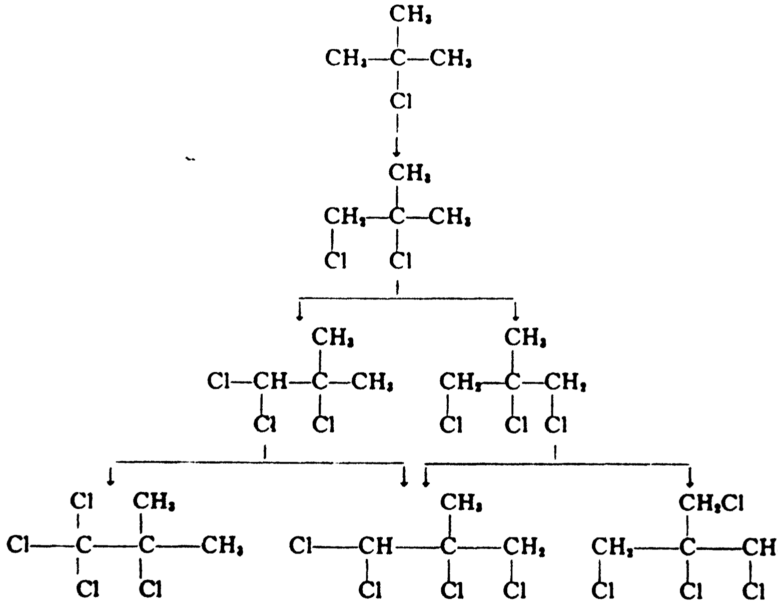
[72a] R. M. Deanesly, British P. 399,991, 1933, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1933, 1046; *Chem. Abs.*, 1934, **28**, 1714.

[72b] L. H. Clark, U. S. P. 2,064,413, Dec. 15, 1936, to Sharples Solvents Corp.; *Chem. Abs.*, 1937 **31**, 708.

According to Nutting, Britton, Huscher and Petrie,[73] *ter*-butyl chloride may be obtained by heating isobutyl chloride (vapor) to 300°C. with a catalyst (anhydrous ferrous chloride) to dissociate it to isobutene and hydrogen chloride. These vapors are passed over aluminum oxide at 150°C. to form the desired product.

Hass, McBee and Weber[74] show that the chlorination of *n*-butane yields 1-chloro and 2-chlorobutane as monochlorides and a mixture of 1,2-dichloro- and 1,3-dichlorobutane as dichlorides, indicating the lack of evidence for carbon skeleton rearrangement such as an isobutyl chloride resulting from the chlorination of *n*-butane.

Further chlorination of 2-chloro-2-methylpropane is reported to lead to a number of chlorine derivatives of isobutane.[75] The halogenation was effected in the liquid phase under a reflux condenser employing ordinary incandescent lamps for activation. The hydrogen chloride formed in the process was absorbed in ice water to prevent loss of the volatile halides. The products secured from the reaction may be represented by



[72c] E. C. Britton, G. H. Coleman and B. C. Hadler, U. S. P. 1,954,438, April 10, 1934, to Dow Chemical Co.; *Chem. Abs.*, 1934, 28, 3739; *Brit. Chem. Abs.* B, 1935, 182. *Cf.* Dutch P. 31,269, 1933, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, 28, 2363.

[73] H. S. Nutting, E. C. Britton, M. E. Huscher and P. S. Petrie, U. S. P. 1,993,719, March 5, 1935, to Dow Chemical Co.; *Chem. Abs.*, 1935, 29, 2549.

[74] H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, 1935, 27, 1191; *J. Inst. Pet. Tech.*, 1935, 21, 449A; *Chem. Abs.*, 1936, 30, 78; *Brit. Chem. Abs.* B, 1935, 1084.

[75] A. O. Roger and R. E. Nelson, *J.A.C.S.*, 1936, 58, 1027; *Chem. Abs.*, 1936, 30, 5175.

Uses of Chlorinated Butane. Among the uses for which monochlorobutane has been proposed is the preparation of butylcellulose.[76] In the procedure, 10 moles of monochlorobutane, 1 mole of mercerized cellulose, and 8 moles of aqueous caustic soda, containing 40-50 per cent of sodium hydroxide, are heated together to 123-125°C. The temperature is maintained at this point for 12 hours. The butylcellulose formed is said to contain 2 butyl groups per molecule and to constitute 80-89 per cent of the theoretical yield. 1,3-Dichloro-2-methyl propane is employed as a diluent in removing wax from mineral oils.[77] 2,3-Dichlorobutane is recommended as a solvent for fats, for its corrosive action on metal containers, while slightly greater than that of dichloroethane, is reported to be less than trichloroethylene.[78] To de-ink paper containing a carbon ink, Hass[79] uses an aqueous soap solution containing 1,3-dichloroisobutane.

FLUORINATION OF BUTANE

Desreux[80] reports the formation of butyl fluoride from butyl iodide and mercurous fluoride, the reaction taking place in a copper flask. According to the above investigator some of the properties of the halide are as follows: boiling point (745.8 mm.) = 31.95-31.98°C., density at 20°C. = 0.7761, indices of refraction, $n_\alpha^{15} = 1.3404$, $n_D^{15} = 1.3419$, $n_\beta^{15} = 1.3457$, $n_\gamma^{15} = 1.3488$ and the viscosity at 20°C. = 0.002845.

CHLORINATION OF PENTANE

To secure monochloro derivatives of pentane, Teichmann, Klein and Rathemacher[81] treat pentane with liquid polychloro hydrocarbons (trichloropentane) by exposure to ultraviolet light. The products are reacted with chlorine under pressure (to prevent inception of a vapor phase) and the monochloropentanes separated from the dichloropentanes by fractionation. At a temperature of 86-90°C., the pentane fraction of gasoline, combined with chlorine in the proportion 6:1 by volume, yields 90 per cent of monochloropentane. A rise in the concentration of chlorine favored the formation of dichloropentane.[82]

When Wertyporoch[83] chlorinated *n*-pentane he obtained a monochloride boiling at about 97°C., and reported the presence of both primary chlorides of isopentane. Hass and Weber,[84] on the other hand, point out that no derivatives of isopentane can be present in the chlorides obtained from *n*-pentane. They support their contention with two considerations: (a) the very much slower rate of metathesis with potassium iodide shown by the secondary chlorides of *n*-pentane as compared to those of the primary chlorides of isopentane[85] and (b) the fact that the mixtures of anilides derived from the secondary chlorides of *n*-pentane have melting points which correspond exactly to the composition calculated from the rule which states that secondary and tertiary hydrogen atoms are always substituted more quickly than primary.[86] For if any of the chlorides of isopentane were present they would cause the melting points to differ from the values previously determined with varying proportions of the chlorides of *n*-pentane.

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[76] S. N. Ushakov and V. A. Kon'kova, *Plasticheskie Massui*, 1934, No. 5, 1; *Chem. Abs.*, 1935, **29**, 3151; *Brit. Chem Abs.* B, 1935, 1135.

[77] L. D. Jones, U. S. P. 2,053,337, Sept. 8, 1936, to Sharples Specialty Co.; *Chem. Abs.*, 1936, **30**, 7321. British P. 445,908, 1936; *Chem. Abs.*, 1936, **30**, 6937. French P. 788,328, 1935; *Chem. Abs.*, 1936, **30**, 1553.

[78] M. V. Likhosherstov, S. V. Alekseev and T. V. Shalaeva, *J. Chem. Ind.* (*Moscow*), 1935, **12**, 705; *Chem. Abs.*, 1935, **29**, 8174.

[79] H. B. Hass, U. S. P. 1,990,376, Feb. 5, 1935, to Purdue Research Foundation; *Brit. Chem. Abs.* B, 1936, 15; *Chem. Abs.*, 1935, **29**, 1986.

[80] V. Desreux, *Bull. sci. acad. roy. Belg.*, 1935, **44**, 1; *Chem. Abs.*, 1935, **29**, 2505.

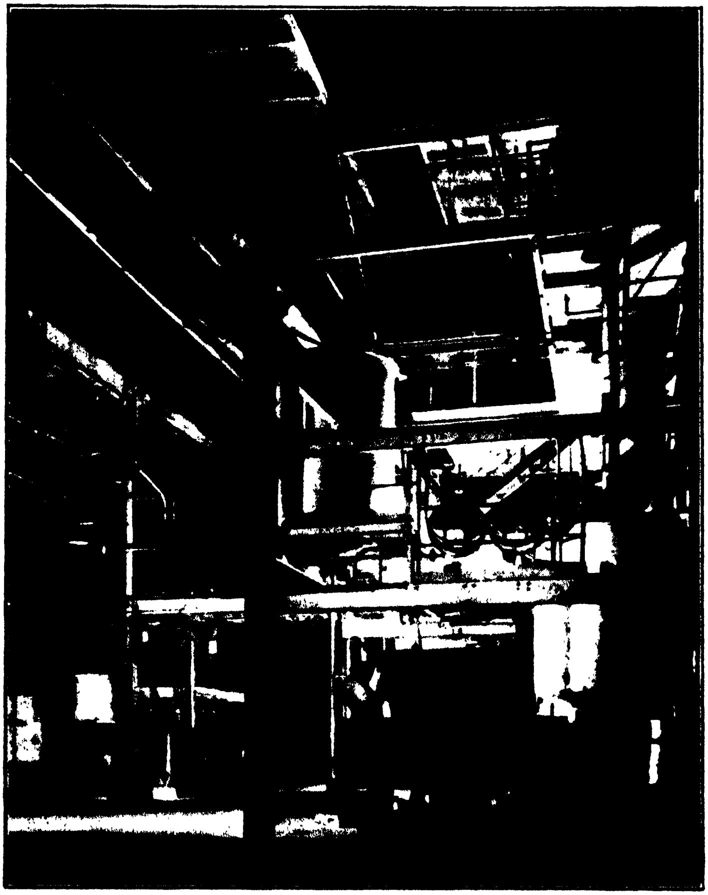
[81] C. F. Teichmann, H. Klein and C. P. Rathemacher, U. S. P. 2,015,044, Sept. 17, 1935; *Chem. Abs.*, 1935, **29**, 7342.

[82] A. Dobryanskii, M. Davuidova and E. Margules, *J. Applied Chem.* (*U.S.S.R.*), 1933, **6**, 1122; *Brit. Chem. Abs.* B, 1934, 231; *Chem. Abs.*, 1934, **28**, 4035.

[83] E. Wertyporoch, *Ber.*, 1933, **66**, 732; *Chem. Abs.*, 1933, **27**, 3443; *Brit. Chem. Abs.* A, 1933, 590.

[84] H. B. Hass and P. Weber, *Ber.*, 1934, **67**, 974; *Brit. Chem. Abs.* A, 1934, 863; *Chem. Abs.*, 1934, **28**, 5038.

[85] H. B. Hass and P. Weber, *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 231; *J. Inst. Pet. Tech.*, 1935, **21**, 372A; *Brit. Chem. Abs.* A, 1935, 1103; *Chem. Abs.*, 1935, **29**, 5774.



Courtesy Dow Chemical Co.

FIG. 162.—View of Plant for Hydrocarbon Chlorination.

Whitmore and Fleming[87] report that when neopentane (tetramethylmethane) and chlorine are allowed to react by exposure to the rays of a 1,000 watt tungsten lamp, neopentyl chloride, $(CH_3)_3CCH_2Cl$ is formed. It may also be prepared from the same reactants at 0°C. in diffused daylight.

Pure neopentyl chloride has the following properties: f.p. $= -20 \pm 1°C.$, $d_4^{20} =$

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[86] H. B. Hass, E. T. McBee and P. Weber, *Ind. Eng. Chem.*, 1936, **28**, 333; *Chem. Abs.*, 1936, **30**, 2913; *Brit. Chem. Abs.* **A**, 1936, 587; *J. Inst. Pet. Tech.*, 1936, **22**, 202A.

[87] F. C. Whitmore and G. H. Fleming, *J.A.C.S.*, 1933, **55**, 4161; *Brit. Chem. Abs.* **A**, 1933, 1271; *Chem. Abs.*, 1933, **27**, 5715.

0.866, n_D^{20} = 1.4042, b.p. (740 mm.) = 83.5°C., b.p. (750 mm.) = 83.9°C., b.p. (760 mm.) = 84.4°C.

Uses of Chlorinated Pentane. The substitution of chlorine in mixed pentanes leads to the formation, in addition to the paraffin halides, of 3,5,5-trimethylheptene-2 and 3,4,5,5-tetramethylhexene-2.[88] Dichloropentane, containing small proportions of phenol, ethyl alcohol and benzene, has been suggested as a paint and varnish remover.[89] A process for the production of alcohol from pentyl chloride has been reported.[90] The halide is treated with a salt of a non-corrosive fatty acid of high boiling point (sodium stearate) to form the ester of an alcohol. The latter is subsequently recovered by hydrolysis.[91] Also, the halogenated pentane may be admixed with caustic solution and amyl oleate[92] to secure amyl alcohol.[93]

Cracked gasoline, when chlorinated and treated with a lead-sodium alloy, furnishes a metallo-organic derivative which is said to be valuable as an antiknock agent for automobile fuels.[94] These metallo-organic compounds may be formed by reacting the chlorinated gasoline with magnesium to form a Grignard reagent, which is then united with the lead-sodium alloy. One of the reported advantages of this procedure is that the antiknock compound may be prepared in the gasoline, thus minimizing the danger of industrial poisoning associated with the manufacture of lead compounds employed to suppress knocking.[95]

Chlorinated gasoline has been proposed as a partial solvent for substances used in coating compositions.[96] Thus, aluminum stearate and aluminum hydroxide are incorporated in a quantity of halogenated gasoline sufficient to dissolve a portion of the mixed salt and base and to maintain the remainder in suspension.

Monochloropentane has been reported to be an anisotropic substance.[97] Evidence for this conclusion was obtained by measuring the amount of depolarization of polarized light when the latter was diffused by the halide. It was found, in this instance, that the light was only partially polarized on diffusion.[98]

CHLORINATION OF HIGHER PARAFFIN HYDROCARBONS

The increment in molecular volume upon chlorination of higher paraffins has been utilized to determine the mechanism of reaction.[99] With a paraffin melting at 46-51°C. the increase in molecular volume on halogenation was stated to be directly proportional to the chlorine content of the product. From this the inference was drawn that chlorination of a saturated long chain hydrocarbon is a substitution, rather than an addition, mechanism. Further, halogenation of high-molecular-weight paraffins was reported to result in a pronounced lowering of the melting point and increase in viscosity of the product.[100]

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[88] N. L. Drake, G. M. Kline and W. G. Rose, *J.A.C.S.*, 1934, **56**, 2076; *Brit. Chem. Abs.* **A**, 1934, 1329; *Chem. Abs.*, 1935, **29**, 113.

[89] M. M. Wilson, U. S. P. 1,918,224, July 7, 1933, to Sharples Solvents Corp.; *Brit. Chem. Abs.* **B**, 1934, 413; *Chem. Abs.*, 1933, **27**, 4642.

[90] British P. 119,249, 1917, to E. I. du Pont de Nemours & Co.; *J.S.C.I.*, 1918, **37** (22), 717A; *Chem. Abs.*, 1919, **13**, 134.

[91] See also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[92] C. L. Campbell, U. S. P. 1,953,745, April 3, 1934, to E. B. Badger & Sons Co.; *Chem. Abs.*, 1934, **28**, 3740; *Brit. Chem. Abs.* **B**, 1935, 138.

[93] For further treatment of the hydrolysis of alkyl halides, see Chapter 33, this text.

[94] S. Shappirio, U. S. P. 2,012,356, Aug. 27, 1935; *Chem. Abs.*, 1935, **29**, 6752; *Brit. Chem Abs.* **B**, 1936, 869.

[95] See also, Chapter 34, this text

[96] E. H. Bucy, U. S. P. 2,077,875, April 20, 1937, to Atlas Powder Co.; *Chem. Abs.*, 1937, **31**, 4023.

[97] An anisotropic substance is one which exhibits the property of double refraction. See E. M. Chamot and C. W. Mason, "Handbook of Chemical Microscopy," John Wiley & Sons, Inc., New York, 1931, 276. *Cf.* J. W. McBain, in J. Alexander, "Colloid Chemistry," The Chemical Catalog Co., Inc., New York, 1926, 1, 137.

[98] E. Canals and P. Peyrot, *Bull. soc. chim.*, 1933, **53**, 741; *Chem. Abs.*, 1934, **28**, 944; *Brit. Chem. Abs.* **A**, 1933, 1229.

[99] Y. Tanaka, R. Kobayashi and I. Nishi, *J. Soc. Chem. Ind., Japan*, 1934, **37**, Suppl. binding 208; *Chem. Abs.*, 1934, **28**, 5399; *Brit. Chem. Abs.* **A**, 1934, 866.

Tanaka, Kobayashi and Furihata[101] plotted the chlorination curves of liquid paraffins to relate reaction time, temperature and the amounts of hydrogen chloride formed. They pointed out that these reactions show an induction period, a gradual increase in the velocity, a maximum reaction velocity, and a sharp decrease in speed to a constant value. This indicates a chain mechanism consisting of a period of activation and one of chain reaction, with the maximum velocity at the transition point of the two.

Formation of resins by chlorination of petroleum tar and subsequent removal of the halogen as hydrochloric acid have been effected.[102] For example, a cracked tar boiling between 330° and 600°F. at 1 mm. was chlorinated at 72-150°F. until the weight of the paraffin increased 10-15 per cent. The chlorinated product was distilled at 660°F. at 760 mm. and then at the same temperature under a pressure of 1 mm. The overhead was said to consist mainly of hydrochloric acid and the oily constituents of the halogenated tar. The residue was cooled to 200°F. and extracted with naphtha to remove the resinous products.

A liquid paraffin from the refining of a Russian engine oil, when combined with chlorine, furnishes a mono-chlor substitution derivative.[103] The product is heavier and more viscous than the original oil, yellowish-green in color, odorless and tasteless. Gallsworthy[104] secured a saturated halide by subjecting lubricating oil to the action of a mixture of hydrochloric and hypochlorous acids at 150°F. (65°C.) under a pressure of 25 pounds per square inch. In the procedure, water and chlorine are admixed in equivalent proportions to form chlorine water (a mixture of hydrochloric and hypochlorous acids). The latter is then conducted to a reaction chamber where it is united with the oil under the conditions mentioned above. The products of the reaction are conducted to a settling chamber where the partially used chlorine water is separated. This chlorine water may be employed to halogenate in part another portion of the oil. (See Fig. 163.) Barth[105] utilizes the reaction of chlorine and a liquid paraffin to secure a substituted halide. The two are united at 180°F. over water containing magnesium or calcium carbonate; the purpose of the latter is to unite with the hydrochloric acid liberated.

Sulphur dioxide and chlorine have been employed to effect the preparation of a halogen derivative of a paraffin wax which was assumed to consist mainly of tetracosane, $C_{24}H_{50}$. Thus, the paraffin was heated to 90-95°C. and a mixture of sulphur dioxide and chlorine bubbled through the resulting liquid.[106] When the weight of the paraffin had increased 20-25 per cent, the temperature was reduced to 40-50°C. for further chlorination. The product was a moderately viscous oil, light yellow in color, and liquid at 20°C. The presence of sulphur dioxide was said to promote substitution on adjacent carbon atoms, so that the resulting paraffin halide could be hydrolyzed to a polyhydric alcohol.

To chlorinate the isomers of hexane and octane in a mixture of normal and

[100] Y. Tanaka, R. Kobayashi and I. Nishi, *J. Soc. Chem. Ind., Japan*, 1934, **37**, Suppl. binding 209; *Chem. Abs.*, 1934, **28**, 5399; *Brit. Chem. Abs.* A, 1934, 866.

[101] Y. Tanaka, R. Kobayashi and M. Furihata, *J. Soc. Chem. Ind., Japan*, 1936, **39**, Suppl. binding 59; *Brit. Chem. Abs.* B, 1936, 435; *Chem. Abs.*, 1936, **30**, 4385.

[102] S. C. Fulton, U. S. P. 1,981,824, Nov. 20, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 589; *Brit. Chem. Abs.* B, 1935, 1005.

[103] E. André and A. Maurel, *Ann. combustibles liquides*, 1935, 10, 807; *J. Inst. Pet. Tech.*, 1936, **22**, 143A; *Brit. Chem. Abs.* B, 1936, 728; *Chem. Abs.*, 1936, **30**, 1217.

[104] B. Gallsworthy, U. S. P. 2,022,619, Nov. 26, 1935, to Texas Co.; *Chem. Abs.*, 1936, **30**, 847; *Brit. Chem. Abs.* B, 1936, 1192.

[105] E. J. Barth, U. S. P. 1,953,286, April 3, 1934, to Sinclair Refining Co.; *Brit. Chem. Abs.* B. 1935, 90; *Chem. Abs.*, 1934 **28**, 3888.

[106] C. F. Reed, U. S. P. 2,046,090, June 30, 193, one half to C. L. Horn; *Chem. Abs.*, 1936, **30**, 5593.

isomeric types, Moldavskii and Livshitz[107] recommend a 0.5*N* solution of antimony pentachloride in chloroform. This will react with the isohexanes and isoöctanes, but not with the *n*-paraffins. A process for preparing pure alkyl chlorides of high molecular weight from the corresponding aliphatic alcohols is reported by Schrauth,[108] who states that all chloro-paraffins with an even number of carbon atoms, from octyl to docosyl (C_{22}) have been synthesized. These higher-molecular halogen alkyls are water-white oils of high boiling point and relatively high flash point, and can be heated to 250-300°C. without decomposition. The density of the oils diminishes with increase in molecular weight and varies between 0.875 and 0.860.

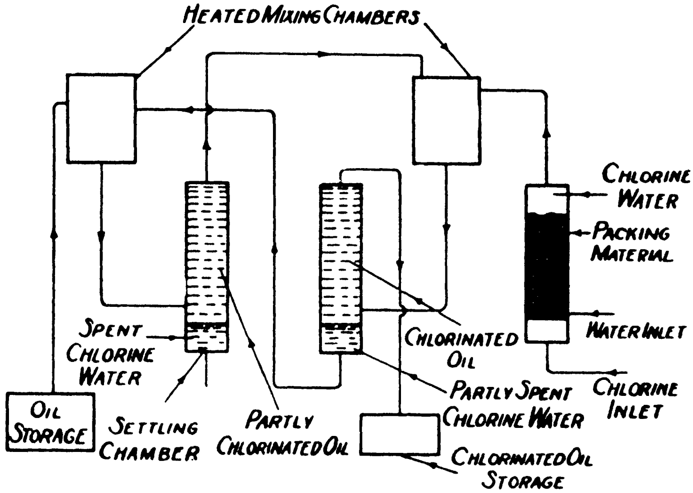

FIG. 163.—Diagram of Method for Chlorination of Hydrocarbon Oils. (B. Gallsworthy)

Properties of Higher Chlorinated Paraffins. Strauss[109] compared the chlorine compounds obtained from soft with those from hard paraffin waxes and found that for the same percentage of chlorine the products from soft wax have lower specific gravities, viscosities and flash-points than those obtained from hard waxes. For both classes these properties increase with further chlorination. The chlorinated waxes are miscible in all proportions with heavy oils, and promote the solubility of castor oil in mineral oils.

Uses of Chloro Derivatives of Higher Paraffin Hydrocarbons. Herbsman[110] reports the use of "chlorocosane" (chlorinated paraffin wax) for breaking petroleum emulsions. A small quantity of the former is added to the emulsion, and the resulting composite is electrically dehydrated.

A method of manufacturing lubricants consists of separation of a mixture of hard or soft paraffins of high carbon content into two fractions with different mean molecular weights. Halogenation and subsequent condensation by the action of a catalyst (e.g., alumina)[111] bring about the formation of the lubricant. A small portion of a synthetic oil, obtained by condensing chlorinated paraffin wax and benzene in the presence of a contact agent (aluminum chloride) is added to heavy transmission gear lubricants to increase the effectiveness of the latter.[112] This synthetic product (of the "Paraflow" type) is recommended by Anderson[113] for dewaxing oils of large molecular weight. The separation of the more active "Paraflow" from the remaining reaction products is said to be accomplished by extraction with a wax precipitant such as butanol or pentanol.[114] Zimmer, Davis and Frolich[115] report that small amounts of wax cause congealing of oil at relatively high temperatures by a twofold action: (a) interlocking wax crystals prevent the free flow of the lubricant and (b) they retain adsorbed oil, causing the formation of a type of gel. The action of "Paraflow" consists in its adsorption on the surface of the wax particles, inhibiting the growth of larger crystals of the latter and causing it to lose its attraction for the oil. "Paraflow" lowers the pour point of Diesel fuels of low paraffin content to −30°C. if an excess of aromatic oils with high melting points is not present.[116] Condensation of diphenylene oxide with a chlorinated paraffin in the presence of aluminum chloride is recommended to prepare a pour point depressant for lubricating oil.[117] In some cases, metallic aluminum is employed to effect condensation.[118] Thus, chlorinated decane is treated with benzene or naphthalene in the presence of the above catalyst to secure a colored substance which is said to impart fluorescence to lubricating oils. To procure wetting and emulsifying agents, Keller and Gofferjé[119] treated polychlorinated hydrocarbons with alkalies and sulphonates, obtaining products containing sulphonic and bisulphate groups. A high or "extreme" pressure lubricant of one process comprises mineral lubricating oil, free sulphur and chlorinated paraffin wax.[120] Also, chlorinated hexane is stated to improve the lubricating properties of mineral oil.[121] Chlorinated hydrocarbons containing more than 9 carbon atoms and at least 2 halogen atoms in a molecule may be reacted with alkalies to obtain a drying oil.[122] For example, a chlorinated solid paraffin having a molecular weight of 367 and containing 14 atoms of chlorine per molecule was heated for 10 hours in an autoclave with aqueous calcium hydroxide. At the end of the reaction period, the products were cooled to 20°C. and the oil separated from the alkaline solution. The oil was then washed with slightly acidulated water and dried. On exposure of the oily product in a thin layer in the air, an elastic film of high luster was said to be secured. Monohalogenated paraffin wax may be reacted with a mixture of potassium acetate and acetic acid, or potassium stearate, butanol and sodium iodide, or of dibutylamine and xylene to yield plasticizing or impregnating agents.[123]

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[107] B. L. Moldavskii and S. E. Livshitz, *Compt. rend. acad. sci.* (*U.R.S.S.*), 1935, 1, 507; *Brit. Chem. Abs.* A, 1935, 728; *Chem. Abs.*, 1935. 29, 4731.

[108] W. Schrauth, *Chem.-Ztg.*, 1934, 58, 877; *Brennstoff-Chemie*, 1934, 15, 473; *Brit. Chem. Abs. B*, 1934, 1049; *Chem. Abs.*, 1935. 29, 2505.

[109] R. Strauss, *Oel, Kohle, Erdoel, Teer*, 1935, 11, 83; *J. Inst. Pet. Tech.*, 1935, 21, 127A; *Chem Abs.*, 1935, 29, 7935.

[110] A. M. Herbsman, U. S. P. 1,931,112, Oct. 17, 1933, to Industrial Patents, Ltd.; *Brit. Chem. Abs.* B, 1934, 748; *Chem. Abs.*, 1934, 28, 307. For preparation of "chlorocosane," see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

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[111] French P. 766,516, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 7519. For a discussion of the refining and properties of lubricants, see A. R. Bowen, *J. Inst. Pet. Tech.*, 1934, **20**, 419; *J. Inst. Pet. Tech.*, 1934, **20**, 408A; *Chem. Abs.*, 1934, **28**, 4581.

[112] G. M. Maverick, British P. 396,147, 1933, to Standard Oil Development Co.; *Chem. Abs.*, 1934, **28**, 632. *Cf.* H. Rohe, German P. 603,269, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 596. P. K. Frolich, U. S. P. 2,015,748, Oct. 1, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 8320; *Brit. Chem. Abs.* **B**, 1936, 1139. Dutch P. 63,597, 1932, to Standard Oil Development Co.; *J. Inst. Pet. Tech.*, 1935, **21**, 28A. Y. Tanaka and R. Kobayashi, Japanese P. 109,419, 1935; *Chem. Abs.*, 1935, **29**, 4574. K. S. Ramayya and S. Khaiman, *Neft. Khoz.*, 1934, **26** (12), 37; *Chem. Abs.*, 1935, **29**, 4928. A. Berne-Allen, U. S. P. 2,008,674, July 23, 1935, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1936, 779; *Chem. Abs.*, 1935, **29**, 6043. O. M. Reiff, U. S. P. 2,052,003, Aug. 25, 1935, to Socony-Vacuum Oil Co.; *Chem. Abs.*, 1936, **30**, 6940. M. T. Flaxman, U. S. P. 2,010,297, Aug. 6, 1935, to Union Oil Co. of Calif.; *Brit. Chem. Abs.* **B**, 1936, 750; *Chem. Abs.*, 1935, **29**, 6333. G. H. B. Davis, U. S. P. 2,062,354, Dec 1, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1937, **31**, 853. *Cf.* F. H. MacLaren and T. E. Stockdale, U. S. P. 2,057,104, Oct. 13, 1936, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1936, **30**, 8600.

[113] J. A. Anderson, U. S. P. 1,998,648, April 23, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 222A; *Chem. Abs.*, 1935, **29**, 3822. British P. 456,422, 1936, to Standard Oil Development Co., *J. Inst. Pet. Tech.*, 1937, **23**, 31A; *Brit. Chem. Abs.* **B**, 1937, 16.

[114] R. G. Sloane, U. S. P. 2,045,806, June 30, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 5782.

[115] J. C. Zimmer, G. H. B. Davis and P. K. Frolich, *Penn. State Coll., Min. Ind. Expt. Sta. Bull.*, 1933, **12**, 57; *J. Inst. Pet. Tech.*, 1934, **20**, 232A; *Chem. Abs.*, 1934, **28**, 2512; *Brit. Chem. Abs.* **B**, 1934, 662.

[116] A. I. Doladugin, M. A. Solodovnik and B. A. Englin, *Neft. Khoz.*, 1935, **28** (4), 68; *J. Inst. Pet. Tech.*, 1936, **22**, 163A; *Chem. Abs.*, 1936, **30**, 3988.

[117] F. Hofmann and E. Dietzel, German P. 626,602, 1936, to Oberschlesischer Berg- und Huttenmannischer Verein e. v.; *Chem. Abs.*, 1936, **30**, 5782.

[118] A. W. Nash, T. G. Hunter and W. R. Wiggins, British P. 447,778, 1936; *Chem. Abs.*, 1936, **30**, 7324.

[119] K. Keller and E. Gofferjé, German P. 622,296, 1935, to I. G. Farbenind. A.-G.; *Chem Abs.*, 1936, **30**, 1467.

[120] British P. 431,434, 1935, to Standard Oil Development Co.; *J. Inst. Pet. Tech.*, 1935, **21**, 382A; *Brit. Chem. Abs.* **B**, 1935, 794.

[121] C. F. Prutton, U. S. P. 2,051,744, Aug. 18, 1936, to Lubri-Zol Development Corp.; *Chem. Abs.*, 1936, **30**, 6939. Similar use of chlorocyclohexane and of pinene hydrochloride has been proposed. See B. H. Lincoln and A. Henriksen, U. S. P. 2,063,880, Dec. 8, 1936; W. L. Steiner, U. S. P. 2,063,857, Dec. 8, 1936, both to Lubri-Zol Development Corp.; *Chem. Abs.*, 1937, **31**, 852.

Also, it has been suggested that the addition of a small proportion of chlorinated paraffin with a molecular weight above 200 to castor oil will render the latter soluble in mineral oil.[124] A coating composition applicable to metals is reported to be furnished by admixing 20 parts of chlorinated rubber and 15 parts of chlorinated paraffin in 65 parts of carbon tetrachloride.[125]

BROMINATION OF HIGHER HYDROCARBONS

According to André and Maurel[126] the bromination of liquid paraffins is more difficult than chlorination, and at best only two-thirds of the theoretical amount of bromine necessary to form a monobromo substitution product can be introduced. Attempts to accelerate the halogenation with various metals were unsuccessful. The product was a brown viscous liquid, which, on standing in a stoppered flask, deposited a powder redissolvable on shaking at 30-35°C. This powder contained 33.5 per cent of bromine, corresponding to a replacement of two hydrogen atoms in a substance of a mean molecular weight of 380.

Uses. Whitmore, Stehman and Herndon[127] report a yield of 10 per cent hexamethylethane from pentamethylethyl bromide in a xylene solution of methylmagnesium chloride (Grignard Reagent) and one of 50 per cent from the same bromide in a xylene solution of zinc dimethyl. The product was employed in studying intramolecular arrangement.

FLUORINATION OF HIGHER HYDROCARBONS

Paraffin wax is fluorinated by treatment, at the boiling point of the solvent (benzene), of a chlorinated solid paraffin with antimony trifluoride and antimony pentachloride, avoiding an excess of the fluoride. The resulting halide is a chemically stable liquid which may be used as a dielectric.[128] Also, it has been stated that a mixture of petroleum hydrocarbons may be fluorinated by conducting a finely divided solution of fluorine gas into the petroleum.[129] The fluorine is prepared by electrolyzing fused potassium bifluoride which contains less than 0.05 per cent of water.

[122] British P. 372,784, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 3742; *Brit. Chem. Abs.* **B**, 1932, 714.

[123] British P. 453,522, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, **31**, 1125; *Brit. Chem. Abs.* **B**, 1936, 1194.

[124] I. Davidsohn and R. Strauss, German P. 608,973, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 296A; *Chem. Abs.*, 1935, **29**, 5297. R. Strauss, *Seifensieder-Ztg.*, 1935, **62**, 238; *Chem. Zentr.*, 1935, 1, 4003; *Brit. Chem. Abs.* **B**, 1936, 557; *Chem. Abs.*, 1935, **29**, 3543.

[125] W. D. Bowlby, U. S. P. 2,057,999, Oct. 20, 1936, to Hercules Powder Co.; *Chem. Abs.*, 1937, **31**, 290.

[126] E. André and A. Maurel, *Ann. combustibles liquides*, 1935, **10**, 807; *J. Inst. Pet. Tech.*, 1936, **22**, 143A.

[127] F. C. Whitmore, C. J. Stehman and J. M. Herndon, *J.A.C.S.*, 1933, **55**, 3807; *Brit. Chem. Abs.* **A**, 1933, 1138; *Chem. Abs.*, 1933, **27**, 5051.

[128] British P. 443,340, 1935, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs.* **B**, 1936, 487; *Chem. Abs.*, 1936, **30**, 5333. The dielectric properties of fluorinated paraffin wax are described in *Chem. Trade J.*, 1936, **98**, 306; *J. Inst. Pet. Tech.*, 1936, **22**, 360A.

[129] O. T. Krefft, British P. 452,656, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, **31**, 1042; *Brit. Chem. Abs.* **B**, 1936, 1140; *J. Inst. Pet. Tech.*, 1936, **22**, 515A.

Chapter 31

Halogenation of Cycloparaffins

Halogenation of the cycloparaffin hydrocarbons occurring in crude petroleum apparently has not been investigated to the same extent as that of the straight chain and aromatic compounds. A possible reason for the scarcity of information may be that the proportion of such saturated cyclic hydrocarbons in many crude petroleums, or their distillates, is much less than that of either paraffins or aromatics. Furthermore, separation of individual cycloparaffins from other admixed hydrocarbons is a difficult operation. Most of the available information is the result of work done with a petroleum fraction having a narrow boiling range, generally from Russian or Rumanian oils, and containing a preponderance of one hydrocarbon.[1]

The name naphthene has been applied as a general term to include all saturated cyclic hydrocarbons. Originally this term was meant to specify only those substances which contained a saturated 5-membered or cyclopentane ring. As a matter of convenience, naphthene has been extended to cycloparaffins in general, such as cyclopropane, cyclobutane, cyclopentane, cyclohexane and cycloheptane.

The action of halogens on naphthenes seems to be similar to that with straight chain hydrocarbons and leads to the production of chloro or bromo compounds containing one or more halogen atoms. However, this similarity exists particularly in the 5- and 6-membered rings, for in the case of cyclopropane and cyclobutane and their homologues, halogenation is frequently associated with an addition reaction leading to the rupture of the ring and the formation of halogenated straight chain hydrocarbons. For example, cyclopropane yields not only the monochloro derivative but also 1,3-dichloropropane.

Chlorination of the cyclopentane and cyclohexane rings appears to take place much more readily than does bromination, especially in the presence of sunlight or other actinic light. The reaction appears to be of a cumulative nature, prolonged treatment giving rise to the formation of polychlorinated products. The presence of catalysts also favors multiple substitution. Bromine will replace hydrogen in cyclopentane or cyclohexane if reactions are carried out above 100°C., but the yield of monobromides is rather poor. In the presence of contact agents, such as aluminum bromide or iron wire, bromination takes place more readily and, if a large proportion of bromine is employed, frequently converts cyclohexane hydrocarbons into polybrominated derivatives of benzenoid hydrocarbons. Furthermore, chlorine and bromine derivatives of the naphthenes may be prepared from the corresponding alcohol by the action of hydrochloric or hydrobromic acids, phosphorus pentachloride or bromide, and phosphorus trichloride or bromide. Addition of bromine or chlorine to an unsaturated naphthene, such as cyclopentene or cyclohexene, will likewise result in the formation of halocycloparaffins.

The substituted derivatives of the naphthenes exhibit a degree of reactivity which is comparable to that of the halogen derivatives of the straight chain hydrocarbons. For example, they may be hydrolyzed to yield a secondary alcohol, decomposed to unsaturated naphthenes by the action of quinoline, converted into cycloalkylamines by reaction with aniline, or combined with magnesium to form Grignard reagents.

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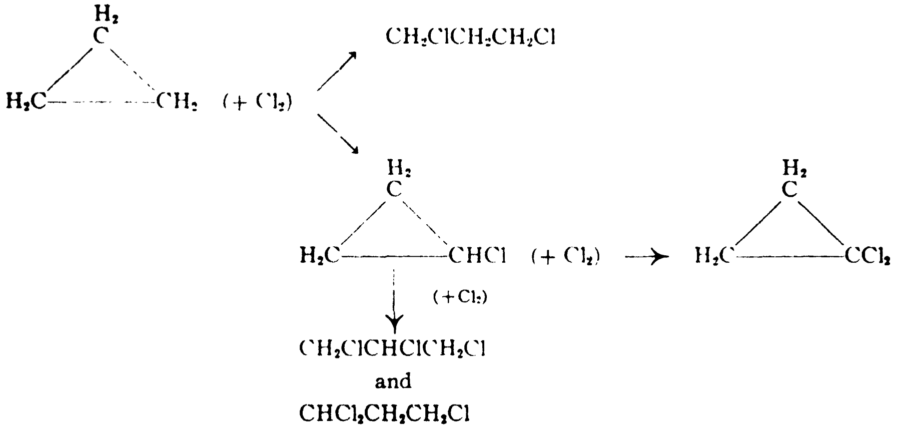
[1] See, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

CYCLOPROPANE

Investigations on the photochemical chlorination of cyclopropane show that although no chlorination occurs in the dark, in direct sunlight the reaction is explosive.[2] Accordingly, diffused daylight has been employed to activate the reactants. Under these conditions the compounds produced included not only mono- and 1,1-dichlorocyclopropanes, but also 1,3-dichloro- and 1,1,3-trichloropropane, showing that there is a tendency of the ring to be ruptured. Halogenation of cyclopropane in diffused daylight may be summarized in the following scheme:



Bromination of cyclopropane in actinic light leads to the formation of a straight chain compound, 1,3-dibromopropane. Halogen carriers, such as aluminum halides, hydrogen bromide, ferric and zinc chlorides, materially increase the rate of addition in the absence of light. In this case also the products consist of 1,3- and 1,2-dibromopropane. It will be seen, therefore, that the cyclopropane ring structure is rather easily ruptured by the action of bromine under the conditions which have been studied.[3] Nicolet and Sattler[4] have proposed a mechanism to account for the addition of bromine when hydrogen bromide is employed as a catalyst. They state that the reaction proceeds by two stages: (1) substitution of bromine in the cyclopropane ring, followed by (2) addition of hydrogen bromide to the substituted naphthene, with a resulting rupture of the ring structure and formation of a dibromopropane.

It is of interest to note that indirect methods have also been proposed for the preparation of halogenated cycloparaffins. For example, cyclopropene is reported to react vigorously with bromine to yield dibromocyclopropane. The reaction is carried out in the cold and in the presence of carbon monoxide, which serves as a diluent.[5] The resulting dihalogenated cyclopropane boils at 45°C. under 27 mm., at 135-136°C. under 743 mm., melts in the range —1° to + 1°C., has d_4^{20} 2.1040 and n_D^{20}1.5369.

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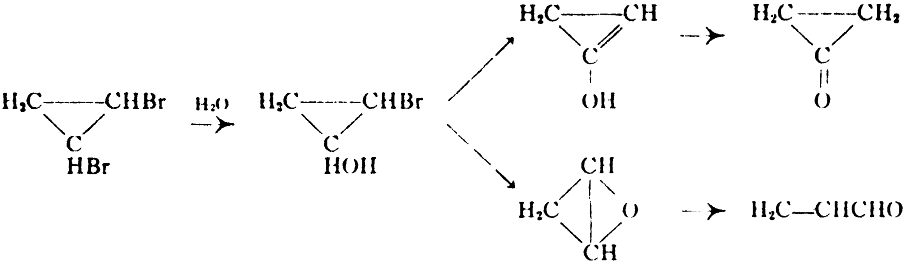
[2] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[3] The relative instability of rings of less than 5 or 6 members is indicated by R. Willstätter and J. Bruce, (*Ber.*, 1907, 40, 4456; *J.C.S.*, 1907, 92 (1), 1018; *Chem. Abs.*, 1908, 2, 398), who stated that the hydrogenation of cyclopropane in the gaseous phase over a nickel catalyst at 120°C. gave propane. In this connection, see Carleton Ellis, "Hydrogenation of Organic Substances," Third Edition, D. Van Nostrand Co., Inc., New York, 1930, Chapter 20.

[4] B. H. Nicolet and L. Sattler, *J.A.C.S.*, 1927, 49, 2066; *Chem. Abs.*, 1927, 21, 3046; *Brit. Chem. Abs.* A, 1927, 1068.

The action of water upon the dibrominated derivatives of cyclopropane does not seem to result in the formation of an alcohol. Dem'yanov and Doyarenko[6] reported that heating dibromocyclopropane with water (in sealed tubes) at temperatures between 105 and 165°C. gives acrolein (acrylaldehyde) and a dark hard substance, insoluble in ether or ethanol and containing 76 per cent of carbon, 6.4 per cent of hydrogen and 17.6 per cent of oxygen. Since this analysis corresponds to the formula C_6H_6O, these investigators believed the solid was formed by the condensation of two molecules of acrolein. A mechanism was proposed to show the action of water on dibromocyclopropane as follows:



When distilled in the presence of zinc dust, dibromocyclopropane is said to lose bromine and form cyclopropene.[7]

CYCLOBUTANE

Apparently very little is known about the halogenation of cyclobutane or its homologues, though this hydrocarbon is said to be stable to halogens in the cold.[8] However, a number of indirect methods for preparing the chlorides or bromides have been proposed and the reactions of the resulting halides have been studied.

Dem'yanov[9] reports that cyclobutanol when treated with concentrated hydrobromic acid at 70°C. for a period of 20 minutes yields a monobromide, C_4H_7Br. This was converted into the magnesium derivative and then reacted with carbon dioxide to furnish a carboxylic derivative said to be cyclopropyl acetic acid. Thus it appears that the ring structure is changed from one of 4 carbons to one of 3 by the action of hydrobromic acid. Cyclobutene does not suffer degradation of the ring structure upon treatment with chlorine or bromine, but readily forms dichloro- and dibromocyclobutane when diffused daylight is employed to energize the reactants.[10] Acids have also been suggested for the preparation of dibromocyclobutane. For example, bromine and caustic potash combine with α-bromotetramethylenecarboxylic acid to furnish cyclobutanone and 1,1-dibromocyclobutane.[11]

Hydrolysis of mono- and dihalocyclobutanes to produce alcohols has not been reported. Kishner[12] states that dibromocyclobutane is converted to cyclobutanone when heated with lead oxide and water at 100°C. The dibromide will react with quinoline to furnish butadiene, and with potassium hydroxide at 210°C. to form acetylene. If the temperature is lowered to 100°C. then 1-bromocyclo-1-butene is furnished. The latter may be oxidized with potassium permanganate in neutral alcoholic solution, and the intermediate product oxidized with chromic acid to succinic acid. The various steps may be represented by:

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[5] N. J. Dem'yanov and M. N. Doyarenko, *Ber.*, 1923, **56**, 2200; *Chem. Abs.*, 1924, **18**, 974; *J.C.S.*, 1923, **124** (1), 1188.

[6] N. J. Dem'yanov and M. N. Doyarenko, *Bull. acad. sci. U.R.S.S., Classe sci. phys. math.*, **1929**, No. 7, 653; *Chem. Abs.*, 1930, **24**, 1848; *Brit. Chem. Abs.* **A**, 1930, 331.

[7] N. J. Dem'yanov and M. N. Doyarenko, *Ber.*, 1923, **56**, 2200; *Chem. Abs.*, 1924, **18**, 974; *J.C.S.*, 1923, **124** (1), 1188.

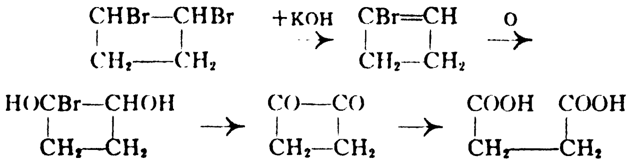
[8] Carleton Ellis, *loc. cit.*

[9] N. J. Dem'yanov, *Ber.*, 1908, 41, 43; *Chem. Abs.*, 1908, **2**, 1123; *J.C.S.*, 1908, **94** (1), 56.

[10] R. Willstätter and J. Bruce, *Ber.*, 1907, 40, 3979; *J.C.S.*, 1907, **92**, 1018; *Chem. Zentr.*, 1907, **2**, 2039.

[11] N. Kishner, *J. Russ. Phys. Chem. Soc.*, 1907, **39**, 922; *Chem. Abs.*, 1908, **2**, 264.

[12] N. Kishner, *loc. cit.*



Dibromocyclobutane is said to react with bromine in the presence of iron with subsequent ring rupture to yield tetrabromobutane.[13] This may be further brominated in the presence of iron, in which case it splits off a molecule of hydrogen bromide, forming an oily product containing hexabromocyclobutane.

The stability of the cyclobutane ring has been investigated by Rozanov[14] who subjected methylcyclobutane to the action of a number of reagents. When it was agitated with fuming hydrobromic acid for 5 hours, methylcyclobutane reacted to form 2-bromopentane. With hydriodic acid, 2-iodopentane was obtained. Bromine, mixed with the methylcyclobutane in sunlight, gave 1,4-dibromopentane. From these experiments the conclusion was drawn that a ring containing 4 carbon atoms is no more stable to the three reagents mentioned above than was cyclopropane, a 3-carbon ring.[15]

CYCLOPENTANE

The published data on the preparation of halogen derivatives of cyclopentane do not present any methods for the direct chlorination or bromination of this cycloparaffin. Nevertheless, a number of halogen substituted cyclopentanes have been prepared by indirect methods.

Monochlorocyclopentane can be made by heating cyclopentanol with concentrated hydrochloric acid (under reflux) for a period of 3 hours.[16] A trichlorocyclopentane has been obtained from the interaction of monochlorocyclopentene and chlorine, and a tetrachloride by chlorination of cyclopentadiene in chloroform solution at −15°C.[17]

Among the uses which have been suggested for monochlorocyclopentane are included the preparation of methyl cyclopentyl carbinol and of cyclopentene. Edwards and Reid[18] state that the alcohol may be secured by combining the chloride with magnesium to form a Grignard reagent which is then reacted with acetaldehyde. In the procedure, 150 cc. of ether and 18 g. of magnesium turnings were placed in a flask fitted with a reflux condenser. To this was added an ethereal solution of monochlorocyclopentane containing 77 g. of the latter substance. The mixture was cooled, refluxed on a water bath for 1 hour and again cooled, forming cyclopentyl magnesium chloride. A solution of 33 g. of acetaldehyde in ether was incorporated with the Grignard compound and allowed to stand for 12 hours. At the end of that period the mixture was refluxed for 15 minutes, acidified with hydrochloric acid, and the ethereal layer extracted. The ether was distilled off and the residue fractionated, the portion boiling at 85-85.5°C. being retained. The complete reaction may be expressed by the mechanism

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[13] R. Willstätter and J. Bruce, *Ber.*, 1907, **40**, 3979; *J.C.S.*, 1907, **92**, 1018; *Chem. Zentr.*, 1907, **2**, 2039.

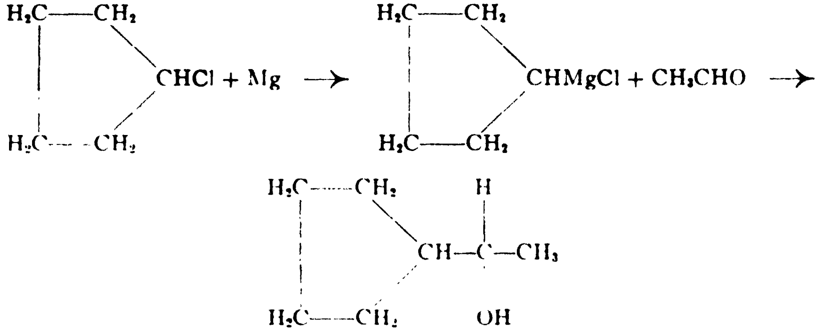
[14] N. A. Rozanov, *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 2291; *Chem. Abs.*, 1930, **24**, 3763; *Brit. Chem. Abs.* **A**, 1930, 587.

[15] The theory of the stability of five or six membered rings is discussed by A. Baeyer (*Ber.*, 1885, **18**, 2269; *J.C.S.*, 1885, **48**, 1198). A discussion of the inevitability of formation of five and six membered rings, and of the fortuity of larger and smaller rings in polymerization is presented by W. H. Carothers, *J.A.C.S.*, 1929, **51**, 2548; *Chem. Abs.*, 1929, **23**, 4438; *Brit. Chem. Abs.* **A**, 1929, 1165.

[16] W. R. Edwards, Jr., and E. E. Reid, *J.A.C.S.*, 1930, **52**, 3235; *Chem. Abs.*, 1930, **24**, 4767; *Brit. Chem. Abs.* **A**, 1930, 1286.

[17] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[18] W. R. Edwards, Jr., and E. E. Reid, *loc. cit.*



The preparation of cyclopentene is said to be effected by conducting chlorocyclopentane vapors, under a pressure of 15 to 20 mm., over a bed of barium chloride which is heated to 300-400°C.[19]

Monobromocyclopentane may be obtained by heating cyclobutylmethanol with hydrogen bromide at a temperature of 100°C.[20] During this operation isomerization of methylcyclobutanol to the corresponding cyclopentane derivative apparently took place. This assumption was further substantiated by reduction of the bromide with zinc and palladium in hydrobromic acid to cyclopentane, b.p. 49-50°C. at a pressure of 750 mm. Noller and Adams[21] point out that cyclopentanol and phosphorus tribromide may be employed to secure monobromocyclopentane. To 172 g. of cyclopentanol, at 0°C., were added 192 g. of phosphorus tribromide, the mixture being stirred to maintain the temperature at 0°C. When incorporation of the latter compound was completed, the temperature was allowed to rise to 20°C. and held at that point for 12 hours. Water was then added and the mixture steam distilled. The distillate separated into two layers, the lower one being removed, dried and fractionated. The cut boiling at 135-136°C. consisted of monobromocyclopentane. Dibromocyclopentane may be prepared by combining cyclopentene and bromine in chloroform[22] or carbon disulphide.[23]

Monobromocyclopentane can be converted into cyclopentyl magnesium bromide in a manner analogous to that employed for the corresponding chloride.[24] By treating this Grignard reagent with formaldehyde, cyclopentyl carbinol is said to be produced. The cyclopentyl magnesium bromide may also be combined with propionaldehyde or butyraldehyde to furnish propyl or butyl cyclopentyl carbinols, respectively.[25]

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[19] O. Schmidt, K. Hochschwender and T. Eichler, U. S. P. 1,221,382, April 3, 1917, to Badische Anilin u. Soda Fabrik; *Chem. Abs.*, 1917, **11**, 1885; *J.S.C.I.*, 1917, **36**, 521.

[20] N. Y. Dem'yanov, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 837; *Chem. Abs.*, 1911, **5**, 3832; *J.C.S.*, 1910, **98** (1), 838.

[21] C. R. Noller and R. Adams, *J.A.C.S.*, 1926, **48**, 1080; *Chem. Abs.*, 1926, **20**, 1598; *Brit. Chem. Abs.* A, 1926, 597.

[22] N. D. Zelinskii and R. Y. Levina, *Ber.*, 1933, **66**, 477; *Chem. Abs.*, 1933, **27**, 3199; *Brit. Chem. Abs.* A, 1933, 495.

[23] M. Godchot and F. Taboury, *Bull. soc. chim.*, 1913, **13**, 535; *Chem. Abs.*, 1913, **7**, 3118.

[24] C. R. Noller and R. Adams, *J.A.C.S.*, 1926, **48**, 1080; *Chem. Abs.*, 1926, **20**, 1598; *Brit. Chem. Abs.* A, 1926, 597.

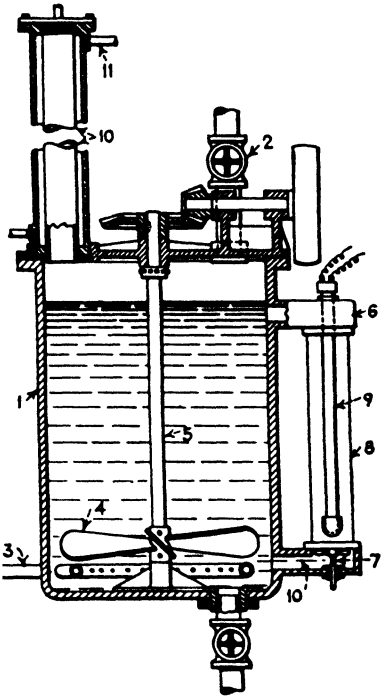
CYCLOHEXANE

Chlorination. Investigations on the chlorination of cyclohexane have revealed that substitution of hydrogen in the cycloparaffin takes place when the hydrocarbon and halogen are exposed to diffused daylight. In this manner mono-, di-, tri- and tetra-chlorocyclohexane have been prepared. Low temperatures (0°C.) should be maintained and the use of catalysts is unnecessary.[26]

1. Vessel for chlorinated hydrocarbon
2. Inlet for hydrocarbon
3. Inlet for chlorine

4, 5. Shaft and propellor
6, 7. Circulating tunnels

8. Glass reaction vessel
9. Mercury vapor lamp
10. Reflux condenser
11. Vent for hydrogen chloride



Courtesy McGraw-Hill Book Co., Inc.

FIG. 164.—Apparatus for Photochlorination Reactions. (P. H. Groggins)

The photochemical reaction between cyclohexane and chlorine in dry carbon tetrachloride has been investigated by Basu.[27] The reactants were subjected to the radiation of a mercury arc lamp, and the course of the reaction was determined by adding potassium iodide to the solution and titrating the liberated iodine with sodium thiosulphate. The velocity constant was reported to be directly proportional to the intensity of the incident radiation and independent of the concentra-

[25] W. R. Edwards, Jr., and E. E. Reid, *J.A.C.S.*, 1930, **52**, 3235; *Chem. Abs.*, 1930, **24**, 4767; *Brit. Chem. Abs.* **A**, 1930, 1206.

[26] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[27] K. P. Basu, *J. Indian Chem. Soc.*, 1929, **6**, 691; *Chem. Abs.*, 1930, **24**, 1023; *Brit. Chem. Abs.* **A**, 1929, 174.

tion of the chlorine. Incorporation of a small proportion of hydrogen chloride in the reaction zone was said to raise the value of the velocity constant. On the other hand, the latter was found to be diminished as the reaction proceeded under these conditions. The retarding influence exercised by the chlorocyclohexane which was formed was offered as a possible reason for the decrease in the velocity constant. The quantum efficiency[28] varied between 19 and 41, being greatest when the wave length of the light employed was 366 millimicrons and least when the wave length was 436 millimicrons. In explanation of the observed facts a mechanism has been suggested which may be represented as follows:

(1) $Cl_2 + h\nu$[a] $\longrightarrow Cl + Cl$
(2) $Cl + C_6H_{12} \longrightarrow C_6H_{11}Cl + H$
(3) $H + Cl_2 \longrightarrow HCl + Cl$
(4) $H + C_6H_{11}Cl \longrightarrow C_6H_{12} + Cl$
(5) $Cl + H \longrightarrow HCl$

[a] $h\nu$ is a quantum of energy.

The fourth equation is offered as an explanation of the cause of the diminution in the velocity constant as the reaction proceeds.

Thermal chlorination of cyclohexane has been recommended as an efficient method for preparing mono- and dichlorocyclohexane.[29] The chlorine and cyclohexane are separately preheated and when the temperature of the reactants has reached 450-550°C. they are forced into a reaction coil at high velocities. The coil in which the two substances are mixed is surrounded by a cooling medium to absorb the heat developed by the interaction. At the end of a contact time of 0.1 second the products are quickly cooled to 20°C. and the mono- and dichlorocyclohexanes are separated by fractionation. The relatively high velocity of the reactants on entering the coils was said to result in thorough mixing of halogen and cycloparaffin, and the short contact time was stated to prevent the occurrence of a flame with an attending deposition of carbon.

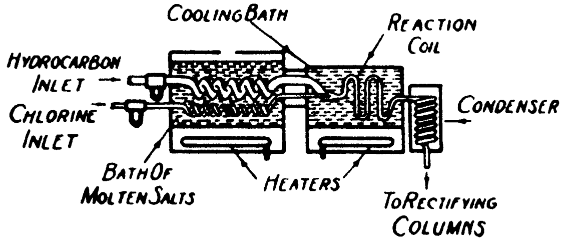


Fig. 165. Method for Thermal Chlorination of Hydrocarbons. (H. B. Hass and E. T. McBee)

Another procedure involves interaction of cyclohexanol with thionyl chloride, employing pyridine as a solvent.[30] In this manner a small proportion of monochlorocyclohexane is said to be obtained, together with a large proportion of cyclohexene. Also, 1,4-cyclohexanediol has been recommended.[31] In the latter case 1 mole of the diol is treated with 3 moles of hydrochloric acid at 100°C. for a period of 6 hours. The main product is 1,4-dichlorohexane together with smaller amounts of 4-chlorocyclohexanol. Chlorination of cyclohexene to 1,2-dichlorocyclohexane has also been advocated.[32]

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[28] Quantum efficiency is the ratio of the number of molecules destroyed to the number of quanta of energy absorbed.

[29] H. B. Hass and E. T. McBee, U. S. P. 2,004,072, June 4, 1935, to Purdue Research Foundation; *Chem. Abs.*, 1935, **29**, 4771.

[30] M. Chaleil, *Bull. soc. chim.*, 1934, 1 (5), 738; *Chem. Abs.*, 1934, **28**, 6711; *Brit. Chem. Abs.* **A**, 1934, 1096.

[31] L. Palfray and B. Rothstein, *Compt. rend.*, 1929, **189**, 701; *Chem. Abs.*, 1930, **24**, 2434; *Brit. Chem. Abs.* **A**, 1929, 1441.

Uses of Chlorocyclohexanes. The chloro derivatives of cyclohexane undergo reactions which are similar to those of the alkyl and aryl chlorides.[33] Monochlorocyclohexane may be converted into a Grignard compound[34] by treating the former with magnesium.[35] Ether is employed as a solvent for the metal, to which monochlorocyclohexane is slowly added while the temperature is maintained at 0°C. When the addition of the chloride is completed, the temperature is raised to 20°C. The product may then be reacted with stannic bromide to form organometallic compounds. In one case the Grignard reagent is diluted with benzene, cooled to 0°C. in an ice-water bath, and the stannic bromide incorporated in the solution. The latter is then heated under a reflux condenser for 3 hours to form a mixture of tetracyclohexyl tin and hexacyclohexyldistannane.

$$4C_6H_{11}MgCl + SnBr_4 \longrightarrow (C_6H_{11})_4Sn + 2MgCl_2 + 2MgBr_2$$
$$6C_6H_{11}MgCl + 2SnBr_4 \longrightarrow (C_6H_{11})_3Sn{-}Sn(C_6H_{11})_3 + 3MgCl_2 + 3MgBr_2 + Br_2$$

The Grignard compound just described may also be employed to furnish (with carbon dioxide) cyclohexanecarboxylic acid which is reported to be a sedative.[36] Carbon dioxide transforms the cyclohexyl magnesium chloride into magnesium cyclohexanecarboxylate, from which the carboxylic acid may be obtained by treatment with a dilute mineral acid.

Monochlorocyclohexane may also be reacted with cycloparaffins in the presence of aluminum halides.[37] For example, Nenitzescu and Ionescu[38] condensed 365 g. of monochlorocyclohexane with 1300 cc. of cyclohexane, using 400 g. of aluminum chloride as catalyst. The temperature was maintained at 20°C. for a period of 3 days, at the end of which time 96 per cent of the theoretical amount of hydrogen chloride had been evolved. Two layers were formed, the upper consisting of cyclohexane admixed with other hydrocarbons. This mixture was fractionated and yielded two cuts, one boiling at 200-230°C. and containing 190 g., the second boiling at 178-186°C. weighing 63 g. The first fraction was again distilled and yielded a portion boiling at 213-215°C. which was said to be 2,2′-dimethyldicyclopentyl. The lower-boiling cut (from the first operation) was found to contain a mixture of hydrocarbons having the general formula $C_{18}H_{32}$, but the structure of these was not determined. The lower layer of the original reaction products contained all the aluminum salts together with 75 g. of unsaturated hydrocarbons which were reported to be formed by the polymerization of the cyclohexene arising from the loss of hydrogen chloride from monochlorocyclohexane.

The action of caustic soda upon chlorinated cycloparaffin results in the formation of a mixture of alcohols and unsaturated hydrocarbons. In one procedure, dichlorocyclohexane was treated with 30 per cent sodium hydroxide at a temperature of 200-230°C.[39] A mixture of chlorocyclohexanols and intermolecular condensation products formed by cracking (even at these temperatures) of the dichlorocyclohexane was secured. It was stated that the presence of copper catalysts serves to accelerate thermal decomposition. The sodium salts of carboxylic acids, the latter obtained from the oxidation of petroleum oils, may be utilized to interact with monochlorocyclohexane.[40] If the temperature is kept at 120-140°C., all the chlorine is eliminated by heating at 160-170°C. to furnish a liquid which is said to be efficient as a drying oil.

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[32] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[33] The reactions of the alkyl and aryl halides are discussed in Chapters 33 and 34.

[34] W. Borsche and W. Lange (*Ber.*, 1905, **38**, 2766; *J.C.S.*, 1905, **88** (1), 765; *Chem. Zentr.*, 1905, **2**, 1092) point out that bicyclohexyl may be obtained as a by-product in the preparation of the Grignard reagent.

[35] E. Krause and R. Pohland, *Ber.*, 1924, **57**, 532; *Chem. Abs.*, 1924, **18**, 2690; *J.C.S.*, 1924, **126** (1), 579.

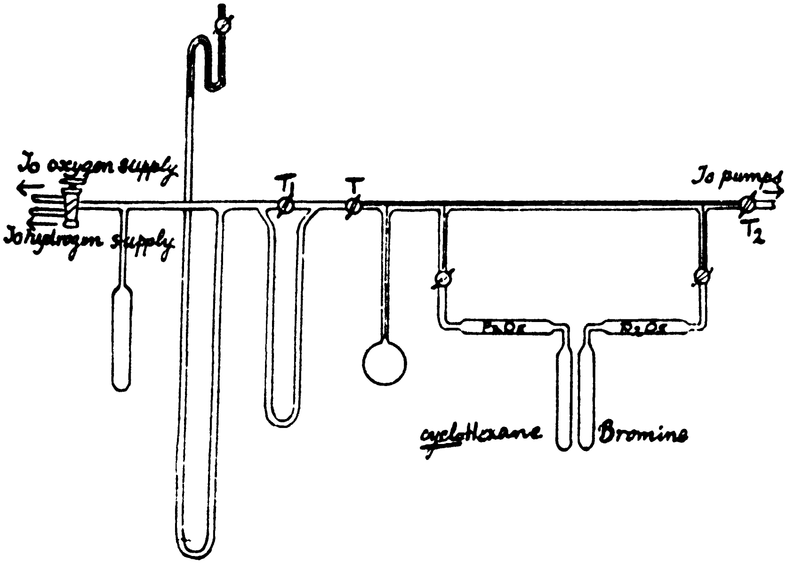
[36] M. E. Fourneau, M. Montaigne and J. Puyal, *Anales soc. españ. fis. quim.*, 1921, **19**, 192; *Chem. Abs.*, 1922, **16**, 240; *J.C.S.*, 1921, **120** (1), 506.

[37] For a discussion of the Friedel-Crafts synthesis, see Chapter 34.

[38] C. D. Nenitzescu and C. N. Ionescu, *Ann.*, 1931, **491**, 189; *Brit. Chem. Abs.* **A**, 1932, 49; *Chem. Abs.*, 1932, **26**, 1256.

[39] A. I. Kiprianov and K. F. Korneich, *Ukrain Khem. Zhur.*, 1936, **11**, Wiss. Tl., 4; *Brit. Chem. Abs.* **B**, 1936, 632; *Chem. Abs.*, 1936, **30**, 7546.

Aniline may be employed to substitute an amino group in a chloro derivative of cyclohexane. For example, it has been suggested that 2 moles of aniline be boiled with 1 mole of monochlorocyclohexane in the presence of copper as a contact agent.[41] On cooling and acidifying with hydrochloric acid, a precipitate of monocyclohexylaniline hydrogen chloride is secured.



Courtesy Journal of The Chemical Society

FIG. 166.—Apparatus Employed for Photobromination of Cyclohexane. (B. J. Wood and E. K. Rideal)

A study of the reaction velocity of monochlorocyclohexane with sodium methoxide (CH_3ONa), pyridine and piperidine has been made by Tronov and Ladigina.[42] They state that the chlorocyclohexane reacts very energetically with the methoxide but less readily than the corresponding aliphatic halides with amines and potassium amides. In its reactivity towards amines, monochlorocyclohexane very greatly exceeds that exhibited by nuclear substituted aromatic halides such as monochlorobenzene. The investigators conclude that there is a similarity between the reactivity of the halogenated cyclohexanes and the tertiary alkyl halides. It is stated that in general chlorine in chlorocyclohexane is not replaced but removed mainly as hydrogen chloride with the production of cyclohexene. The latter compound then undergoes an addition reaction to form a derivative of cyclohexane.

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[40] A. Ya. Drinberg. *Natl. Paint. Varnish and Lacquer Assoc. Circ.*, 1936. **501**, 1; *Chem. Abs.*, 1936, **30**, 3665; *Brit. Chem. Abs.* **B**, 1936, 648.

[41] British P. 261,764. 1925. to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1927, 809; *Chem. Abs.*, 1927, **21**, 3626.

[42] B. V. Tronov and L. V. Ladigina. *Ber.*, 1930, **63**, 3060; *Chem. Abs.*, 1931, **25**, 864; *Brit. Chem. Abs.* **A**, 1931, 207.

Bromination. Bromine may be substituted in cyclohexane when the two compounds are heated to 110°C. in sealed tubes and exposed to diffused sunlight. Also, aluminum bromide may be added as an accelerator, but in this case the cyclohexane ring is converted into one of methylcyclopentane.[43]

The photochemical bromination of cyclohexane has been investigated to determine the dependence of the velocity constant upon various factors and to account for the inhibitory effect of oxygen.[44] The reaction vessel consisted of a glass cylinder connected through capillary tubes to reservoirs containing the bromine and cyclohexane. A pressure gage was employed to measure the extent of reaction, and a mercury lamp to energize the reactants. The light was passed through a vessel with plane parallel glass faces in which cold water was employed to remove the infra-red line. The remaining lines were then filtered through a saturated solution of potassium dichromate, to which neodymium magnesium nitrate had been added, to separate the yellow line. In this manner only the mercury green line was allowed to reach the reactants. The reaction rate was stated to be directly proportional to the light intensity and independent of the concentration of cyclohexane. Also, it was pointed out that the velocity of the reaction is reduced by the presence of oxygen and that this inhibitory effect is independent of the presence of the cyclohexane. The conclusion is drawn that not atoms but excited bromine molecules are the primary photoactive constituent. Further, that it is not these excited molecules but excited $C_6H_{12}Br_2$ molecules which are deactivated on collision with oxygen. The mechanism of the photobromination and inhibition by oxygen was accordingly described by the reactions:

$$\begin{array}{lll}
Br_2 & + h\nu & \longrightarrow & Br_2'^{a} \\
C_6H_{12} & + Br_2' & \longrightarrow & C_6H_{12}Br_2' \\
C_6H_{12}Br_2' & & \longrightarrow & C_6H_{11}Br' + HBr \\
C_6H_{12}Br_2' & + O_2 & \longrightarrow & C_6H_{12} + Br_2 + O_2 \\
C_6H_{11}Br' & + Br_2 & \longrightarrow & C_6H_{10}Br_2 + HBr
\end{array}$$

[a] Br' represents an activated bromine molecule.

On the other hand, Jost[45] pointed out that when reactions are carried out in the temperature range 78-106°C., the velocity constants are approximately proportional to the square root of the cyclohexane concentration. However, the velocity was said to be constant during any one experiment. The presence of hydrogen was reported to have no effect upon the speed of the substitution but oxygen greatly retards the reaction.[46] The quantum efficiency was stated to be about 2 at 20°C. and to increase with rising temperatures, being of the order of 12 to 40 between 73 and 100°C.

It is interesting to note that monobromocyclohexane may be prepared from cyclohexanol. In one process,[47] the alcohol is heated to 100-120°C. and dry hydrogen bromide passed in for 1.5 hours. As soon as replacement of the hydroxyl group is complete the products are separated to remove aqueous hydrobromic acid. Concentrated sulphuric acid is then incorporated in the bromide portion to convert any free alcohol to the acid sulphate, which is soluble in 50 per cent methyl alcohol and ammonia and may be removed by these reagents. The yield of monobromocyclohexane is said to be 75 per cent of the theoretical amount. Phosphorus tribromide has been recommended in place of hydrogen bromide for the preparation of monobromocyclohexane in certain instances.[48] Phosphorus tribromide and cyclohexanol in the molecular proportion 1:3 are mixed and allowed to stand at 20°C. for 12 hours. The resulting compounds are duly heated under a reflux condenser for 2 to 3 hours to form a separate aqueous layer containing phosphorous acid which may be removed. The remaining hydrocarbon bromide is then washed with concentrated sulphuric acid and distilled at 760 mm., the portion boiling at 165-166°C. being retained. Also it has been suggested that bromine and cyclohexanol be incorporated in a solvent of carbon tetrachloride to furnish dibromocyclohexane.[49] However in this case the yield is said to be relatively low since tetrabromocyclohexanone is always formed in the same proportion as the dibromide.

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[43] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

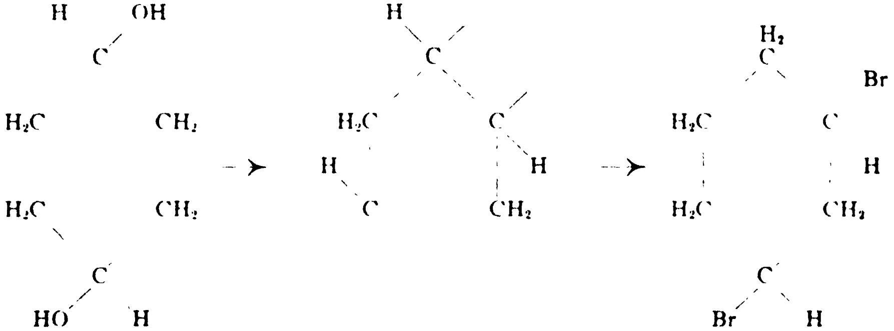
[44] B. J. Wood and E. K. Rideal, *J.C.S.*, **1927**, 2466; *Chem. Abs.*, 1928, **22**, 392; *Brit. Chem. Abs.* **A**, 1927, 1154.

[45] W. Jost, *Z. physik. Chem. Bodenstein-Festband*, **1931**, 291; *Chem. Abs.*, 1931, **25**, 5845; *Brit. Chem. Abs.* **A**, 1931, 1251.

[46] The effect of oxygen in polymerization is discussed in Chapter 26.

[47] E. E. Reid, J. R. Ruhoff and R. F. Burnett, "Organic Syntheses," John Wiley & Sons, Inc., New York, 1935, **15**, 24; *Chem. Abs.*, 1935, **29**, 5067; *Brit. Chem. Abs.* **A**, 1936, 587.

Compounds which contain two hydroxy groups have been utilized to furnish dibromo derivatives of cyclohexane. For example, Rothstein[50] reports that the action of concentrated hydrobromic acid upon 1,3- and 1,4-cyclohexanediol leads to the production of 1,3-dibromocyclohexane. The formation of the latter compound from the 1,4-cyclohexanediol is explained as a "pseudomigration," that is, a hydrogen atom and hydroxyl group split off from adjacent carbon atoms to form water, and that hydrogen bromide is then added to the double bond.



However, Zelinskii and Kozeshkov[51] maintained that the interaction of aqueous hydrobromic acid upon 1,4-cyclohexanediol caused substitution to take place in the 1 and 4 position with a resulting formation of 94 per cent of 1,4-dibromocyclohexane. These investigators stated that a small amount of a solid isomer, either 1,2- or 1,3-dibromocyclohexane, was also secured.

Dibromo derivatives of cyclohexane may be prepared from unsaturated cyclic compounds as for example cyclohexene.[52] Bromine dissolved in carbon tetrachloride is added to a cooled solution (0°C.) of cyclohexene in carbon tetrachloride, the rate of mixing being regulated so that the temperature will not rise above 3°C. When the reaction has been completed, carbon tetrachloride and excess cyclohexane are removed by distillation and the residue is fractionated. The reported yield of 1,2-dibromocyclohexane is 73-86 per cent of the theoretical amount.

[48] Chao-Lun Tseng, May Hsu and Mei Hu, *Science Quart., Natl. Univ. Peking*, 1935, **5**, 371; *Brit. Chem. Abs.* **A**, 1935, 1348; *Chem. Abs.*, 1935, **29**, 6568.

[49] F. Badroux and F. Taboury, *Compt. rend.*, 1912, **154**, 1509; *Chem. Abs.*, 1912, **6**, 2239; *J.C.S.*, 1912, **102** (1), 567.

[50] B. Rothstein, *Ann. chem.*, 1930, **14**, 461; *Chem. Abs.*, 1932, **26**, 99; *Brit. Chem. Abs.* **A**, 1931, 347.

[51] N. D. Zelinskii and K. A. Kozeshkov, *Ber.*, 1927, **60**, 1102; *Chem. Abs.*, 1927, **21**, 2464; *Brit. Chem. Abs.* **A**, 1927, 653.

[52] H. Greengard, "Organic Syntheses," John Wiley & Sons, Inc., New York, 1932, **12**, 26; *Chem. Abs.*, 1932, **26**, 3490.

Reactions of the Bromocyclohexanes. Among the reactions of the bromine derivatives of cyclohexane, the formation of a Grignard reagent through interaction with magnesium has received attention. Gilman and McCracken[53] investigated the reaction between monobromocyclohexane and magnesium to determine the yield of Grignard reagent that could be secured from this halide. Magnesium (1.25 g.) was introduced into a flask, and after all the air had been driven out by a stream of hydrogen gas, ether was then introduced. The mixture was stirred and a solution of 7.69 g. of cyclohexyl bromide in ether slowly incorporated over a period of 45 minutes. The amount of cyclohexyl magnesium bromide produced was stated to be 68.32 per cent of theoretical. One of the possible uses of the Grignard reagent is indicated by Hiers and Adams.[54] They combined magnesium and cyclohexyl bromide in the ratio 1 :1 by moles employing dry ether as a solvent. The Grignard compound was then reacted with methyl λ-aldehydododecanoate ($CHO-(CH_2)_{11}-COOCH_3$) and the product condensed to furnish μ-cyclohexyltridecanoic acid, which is said to be effective in killing *lepra* bacillus. Dihydrochaulmoogric acid, whose ethyl and sodium derivatives are stated to kill

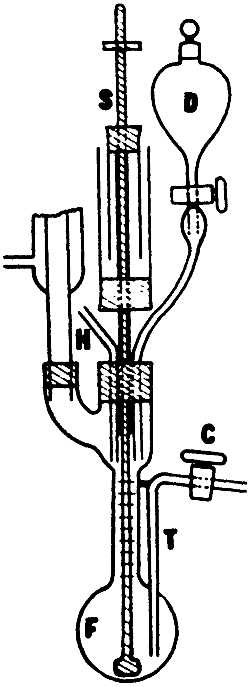
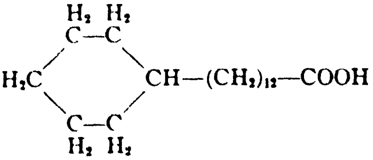


FIG. 167.
Apparatus for Formation of Cyclohexyl Magnesium Bromide. (H. Gilman and R. McCracken)

C. Stopcock
D. Dropping funnel
F. Flask
H. Tube for admitting hydrogen
S Glass stirrer
T. Side tube

Courtesy Journal of American Chemical Society



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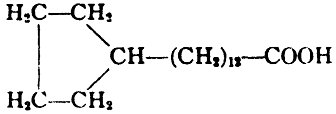
[53] H. Gilman and R. McCracken, *J.A.C.S.*, 1923, 45, 2462; *Chem. Abs.*, 1923, 17, 3859; *J.C.S.*, 1924, 126 (1), 23.

[54] G. S. Hiers and R. Adams, *J.A.C.S.*, 1926, 48, 1089; *Chem. Abs.*, 1926, 20, 1599; *Brit. Chem. Abs.* A, 1926, 597.

this bacillus, have the same straight chain as the acid mentioned above, but contain a cyclopentyl in place of the cyclohexyl ring.



The latter acid may be obtained from the natural chaulmoogra oils, which have been employed in treating leprosy.

Further, the preparation of Grignard reagents from difficultly soluble halides has been investigated. The addition of a small amount of ethyl bromide is said to aid the interaction between monobromocyclohexane and magnesium. Grignard[55] points out that the reason for the successful operation of the ethyl halide was the fact that it cleansed the magnesium and halides. Urion,[56] however, maintains that the main reason for the success of this method is that the ethyl bromide acts as a carrier, according to the equations:

$$C_2H_5Br + Mg \longrightarrow C_2H_5MgBr$$
$$C_2H_5MgBr + C_6H_{11}Br \longrightarrow C_2H_5Br + C_6H_{11}MgBr$$

To demonstrate this, 1 mole of ethyl bromide was treated with an excess of magnesium. The liquid was then decanted from the unreacted magnesium, and 1 mole of monobromocyclohexane added to the former. The two liquids were kept in contact for a period of 24 hours after which the mixture was hydrolyzed. A yield of 10 g. of cyclohexane, corresponding to a 12 per cent yield (by the second reaction above) was obtained. Distillation of 65 per cent of the ether solvent was said to raise the yield of cyclohexane to 40 per cent, since this substance carried off the ethyl bromide as quickly as it was formed.

The bromine derivatives of cyclohexane are utilized in the production of cyclohexylamines. For example, 1 mole of monobromocyclohexane was boiled with 2 moles of aniline in the presence of a copper catalyst.[57] When the solution had been cooled and acidified with hydrochloric acid, a precipitate of monocyclohexylaniline hydrogen chloride was formed. Certain other compounds containing nitrogen will also react with the bromides of cyclohexane. Thus, 1 part of 1,2-dibromocyclohexane is combined with 4 parts of quinoline at 237°C.; cyclo-1,3-hexadiene and 1-monobromocyclo-1-hexene are stated to be obtained.[58]

Potassium phthalimide ($C_6H_4(CO)_2NK$) and 1,4-dibromocyclohexane heated together at 160-165°C. for 8 hours yield 33 per cent of monobromocyclo-3-hexene, which may be isolated by steam distillation.[59] Semb and McElvain[60] have made a study of the reactivity of various normal, secondary and tertiary alkyl halides with piperidine as compared with that of monobromocyclohexane and the same nitrogen compound. They found that the normal or primary alkyl halides reacted completely with the naphthene base in 48 hours. The secondary and tertiary halides were much less disposed to react. Monobromocyclohexane, which may be considered as a secondary halide, is far less reactive than any of the three classes mentioned above. It was suggested, therefore, that the reactivity which the other secondary bromides show may be due to a rearrangement to the more reactive primary bromide, and that the non-reactivity of the cyclohexyl bromide may be attributed to its inability to undergo rearrangement. In a later work[61] it was reported that from *n*-, *iso*-, *sec*- and *ter*-butyl bromides and piperidine, four different N-butylpiperidines are formed. This fact was said to be a definite proof that these bromides interact with piperidine to give tertiary amines without rearrangement. A comparison of the behavior of *sec*-butyl bromide and cyclohexyl bromide upon admixture with piperidine is stated as an indication that the difference in reactivity of these secondary bromides is one of degree rather than kind.

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[55] V. Grignard, *Compt. rend.*, 1934, **198**, 625; *Chem. Abs.*, 1934, **28**, 2692; *Brit. Chem. Abs.* **A**, 1934, 397.

[56] E. Urion, *Compt. rend.*, 1934, **198**, 1244; *Brit. Chem. Abs.* **A**, 1934, 640; *Chem. Abs.*, 1934, **28**, 3721.

[57] G. Kränzlein and M. Corell, German P. 490,715, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, **24**, 4790. British P. 261,764, 1925, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1927, 809; *Chem. Abs.*, 1927, **21**, 3626.

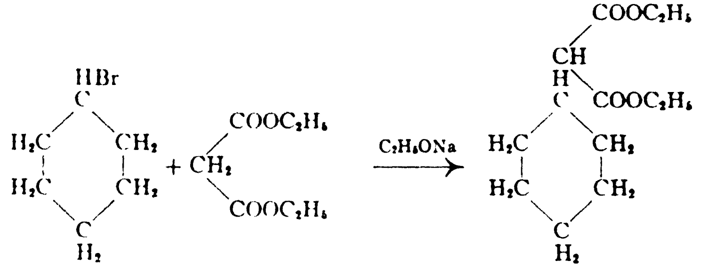
[58] N. Zelinskii and A. Gorskii, *Ber.*, 1911, **44**, 2312; *Chem. Abs.*, 1911, **5**, 3809; *J.C.S.*, 1911, **100** (1), 847.

[59] W. Sobecki, *Ber.*, 1910, **43**, 1038; *Chem. Abs.*, 1910, **4**, 2462; *J.C.S.*, 1910, **98** (1), 366.

[60] J. Semb and S. M. McElvain, *J.A.C.S.*, 1931, **53**, 690; *Chem. Abs.*, 1931, **25**, 1252; *Brit. Chem. Abs.* **A**, 1931, 494.

Also it is interesting to note that when monobromocyclohexane is heated under a reflux condenser for 24 hours with potassium carbonate in water, 8.3 per cent of cyclohexene is formed.[62]

The action of the sodium salts of malonic acid upon monobromocyclohexane leads to a number of products, among them ethyl cyclohexyl malonate.[63] To obtain the latter it has been recommended that sodium be dissolved in alcohol and the solution mixed with ethyl malonate and bromocyclohexane. The composite is then heated on a water bath for 24 hours. Water is incorporated and the product extracted with ether. The latter solution is washed, dried, evaporated, and the residue distilled under a pressure of 20 mm., the fraction boiling at 163-165°C. at this pressure being ethyl cyclohexyl malonate.



Fluorination. The fluorination of cyclohexane has not been reported, but the preparation of fluorinated derivatives by indirect methods has been described. For example, Swarts[64] suggests that monobromocyclohexane be heated with mercurous fluoride in a platinum or copper flask on an oil bath at 130°C. for a period of 5 days. The best yields of monofluorocyclohexane were obtained with the latter apparatus. Under these conditions, 30 per cent of the monofluoride was produced, together with 31 per cent of cyclohexene, 12 per cent of a polymerized product, and some of the original reactants. The use of platinum apparatus increased the amount of polymer to 26 per cent. The mixture of monofluorocyclohexane and cyclohexene was steam-distilled and the unsaturated cyclic hydrocarbon removed (from the distillate) as dibromocyclohexane by adding bromine in aqueous potassium bromide to the cyclohexene at 0°C., in the presence of diffused sunlight. To obtain purified monofluorocyclohexane the mixture was fractionally distilled under 100 mm. pressure, the portion boiling at 43.2°C. being retained. The fluorine derivative had the following properties: melting point, 13°C.; boiling point at 760 mm, 100.2°C.; d_4^{20} 0.9296; n_D^{20} 1.4146. A fluorine derivative boiling at 100°C. has also been secured from the interaction of cyclohexane and fluorine in a solution of difluorodichloromethane at —80°C.[65]

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[61] W. V. Drake and S. M. McElvain, *J.A.C.S.*, 1933, 55, 1155; *Chem. Abs.*, 1933, **27**, 1884; *Brit. Chem. Abs.* **A**, 1933, 512.

[62] J. Loevenich, H. Utsch, P. Moedrickx and E. Schaeffer, *Ber.*, 1929, **62**, 3084; *Chem. Abs.*, 1930, **24**, 1849; *Brit. Chem. Abs.* **A**, 1930, 200.

[63] E. Hope and W. H. Perkins, Jr., *J.C.S.*, 1909, **95**, 1360; *Chem. Abs.*, 1909, **3**, 2965.

[64] F. Swarts, *Bull. sci. acad. roy. Belg.*, 1936, **22**, 105; *Brit. Chem. Abs.* **A**, 1936, 712; *Chem. Abs.*, 1936, **30**, 4153.

Properties of Fluorocyclohexane. Swarts[66] has found that monofluorocyclohexane is rather unstable, splitting off hydrogen fluoride to form cyclohexene. This decomposition is reported to be catalyzed by sulphuric acid and phosphorus pentoxide, and autocatalyzed by the hydrogen fluoride which is formed. When treated with sodium, monofluorocyclohexane gave a precipitate of sodium fluoride. Simultaneously, cyclohexene, cyclohexane and a trace of dicyclohexane were formed. All attempts to prepare a Grignard compound with magnesium and ether were said to be fruitless. Bromine in acetic acid reacted slowly with monofluorocyclohexane but it was stated that the hydrogen bromide liberated accelerated the elimination of hydrogen fluoride, so that the main portion of the products consisted of dibromocyclohexane, together with a trace of a bromofluorocyclohexane which boils at 80°C. under a pressure of 30 mm.

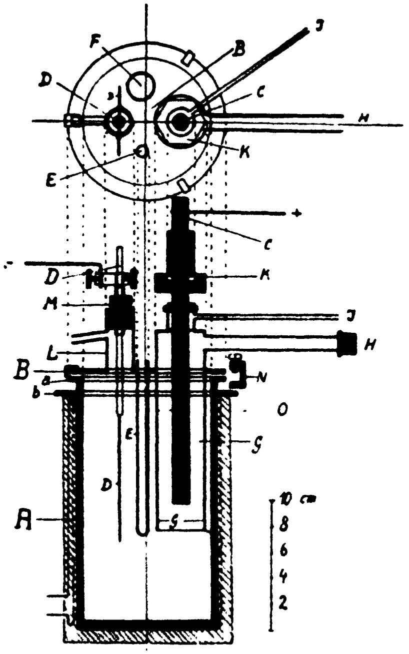

FIG. 168.
Drawing of Apparatus for Fluorination Reactions. (W. Bockemüller)

A. Copper vessel
B. Cover
C. Graphite anode
D. Copper cathode
E. Thermometer tube
F. Safety tube
G. Diaphragm
H. Delivery tube
J. Copper tube
K. Screw lock
L. Cathode cover
M. Lining
N. Clamp

a; b. copper rim

Courtesy Verlag Chemie G.m.b.H

Iodination. Reaction between iodine and cyclohexene, giving rise to iodo derivatives of cyclohexane, has been reported. The reactants were mixed in toluene at 0°C. in the presence of actinic light, and various catalysts, including lead chloride and silver perchlorate, were incorporated.[67] The presence of these catalysts was said to increase the rate of reaction which was determined by titration of the free iodine with sodium thiosulphate. The increase in the velocity depends not only upon the presence of contact agents, but also upon the proportion of the latter,

[65] W. Bockemüller, *Ann.*, 1933, **506**, 20; *Chem Abs.*, 1934, **28**, 118; *Brit. Chem. Abs.* **A**, 1933, 1139.

[66] F. Swarts, *loc. cit.*

[67] L. Birckenbach, J. Gaubeau and H. G. Krall, *Ber*, 1936, **69**, 476; *Brit Chem. Abs.* **A**, 1936, 435; *Chem Abs.*, 1936, **30**, 7053

since greater amounts caused a corresponding rise in the reaction rate. This was reported to indicate the effect is not purely catalytic, but that formation of intermediate mixed halogens also takes place.

HALOGENATION OF HOMOLOGUES OF CYCLOHEXANE

Methylcyclohexane. The direct chlorination (and bromination) of methylcyclohexane at 0°C. in the presence of diffused daylight leads to substitution on the tertiary carbon atom.[68] This seems to be the only halogen substituted product which can be obtained, but a number of halomethylcyclohexanes may be prepared from the corresponding alcohols or unsaturated cyclic compounds.

Methylcyclohexanol is sometimes employed as a reagent for the formation of chloro- and bromoethylcyclohexane. When hydrochloric acid is combined with 1,2-methylcyclohexanol, 1-chloro-2-methylcyclohexane is said to be secured. The product boils at 88°C. under 100 mm. pressure and has d_4^{20} 0.9788.[69] Also, it has been suggested that phosphorus pentachloride be employed instead of hydrochloric acid.[70] An explanation of the formation of the chlorides from the alcohols has been offered by Mailhe and Murat.[71] They consider that the first step in the reaction is a dehydration, resulting in the splitting off of a molecule of water followed by the addition of hydrogen chloride (from the hydrolysis of the pentachloride) to the unsaturated cyclic compounds.

Among the unsaturated cyclic hydrocarbons which have been used to prepare halogen compounds are included 4-bromo-1-methyl-1-cyclohexene and methylcyclohexene. The former substance, when reacted with fuming hydrobromic acid, is reported to yield 1,4-dibromo-1-methylcyclohexane.[71a] Methylcyclohexene, when treated with bromine, furnishes 1,2-dibromo-1-methylcyclohexane. When mixed with bromine to which was added 1 per cent of aluminum, the hydrogen atoms of the cyclic portion are said to be removed, and the product of the reaction consists of pentabromotoluene.[72]

Dimethylcyclohexane. The cyclic hydrocarbons generally employed to prepare the halogen derivatives of dimethylcyclohexane are dimethylcyclohexanol and dimethylcyclohexene. Auwers[73] pointed out that 4-chloro-1,4-dimethylcyclohexane may be obtained from the reaction between 1,4-dimethyl-4-cyclohexanol and phosphorus pentachloride. The product boils at 50-52°C. under a pressure of 14 mm. and has d_4^{20} 0.943. In the same manner, 2-chloro-1,2-dimethylcyclohexane may be secured from 1,2-dimethyl-2-cyclohexanol. The chloride boils at 122.5°C. at 760 mm. and has d_4^{20} 0.779. When 1,3-dimethylcyclohexene is combined with bromine or chlorine a dihalodimethylcyclohexane is formed.[74] The latter substance may be distilled with quinoline and the fraction boiling at 129-130°C. at 745 mm. is said to be 1,4-dimethyl-2,4-cyclohexadiene.

Trimethylcyclohexane. Of the cyclohexane homologues with nine carbon atoms, 1,2,4-trimethylcyclohexane has been isolated from petroleum.[75] Chlorination of this hydrocarbon in the vapor phase, employing dry reagents, resulted in a mixture of monochlorides and dichlorides, whose structures were not determined.

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[68] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[69] J. Gutt, *Ber.*, 1907, **40**, 2061; *Chem. Abs.*, 1907, **1**, 2106; *J.C.S.*, 1907, **92** (1), 508.

[70] M. Murat, *Ann. chim. phys.*, 1909, **16**, 108; *Chem. Abs.*, 1909, **3**, 1275; *J.C.S.*, 1909, **96** (1), 146.

[71] A. Mailhe and M. Murat, *Chem.-Ztg.*, 1911, **35**, 193; *Chem. Abs.*, 1912, **6**, 2406.

[71a] E. Hope and W. Perkin, Jr., *J.C.S.*, 1911, **99**, 762; *Chem. Abs.*, 1911, **5**, 3050.

[72] F. Badroux and F. Taboury, *Bull. soc. chim.*, 1911, **9**, 595; *Chem. Abs.*, 1911, **5**, 3232; *J.C.S.*, 1911, **100** (1), 533.

[73] K. v. Auwers, *Ann.*, 1920, **420**, 84; *Chem. Abs.*, 1920, **14**, 2160; *J.C.S.*, 1920, **118** (1), 721.

[74] N. Zelinskii and A. Gorsky, *Ber.*, 1908, **41**, 2630; *Chem. Abs.*, 1908, **2**, 3082; *J.C.S.*, 1908, **94** (1), 619.

[75] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

Menthane. Chlorination of menthane, or 1-methyl-4-isopropylcyclohexane, in the vapor phase gives rise to a liquid monochloride which boiled at 208-210°C. The constitution of this monochloride is unknown and its homogeneity doubtful. The bromination of menthane has been reported by Schoeller and Borgwardt.[76] They recommend that 21 g. of menthane and a small proportion of iodine be placed in a flask at 0°C. and 24 g. of bromine be slowly poured into the mixture. Hydrogen bromide is evolved, and when this evolution is complete, the remaining products may be washed with water and a solution of sodium carbonate. To isolate the monobrominated menthane, the mixture is distilled under 15 mm. pressure, and the portion boiling at 115-120°C. is retained.

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[76] W. Schoeller and E. Borgwardt, U. S. P. 1,916,742, July 4, 1933, to Schering-Kahlbaum A.-G.; *Chem. Abs.*, 1933, **27**, 4547.

Chapter 32

Halogenation of Benzene and Its Immediate Homologues

Although benzene and other aromatic hydrocarbons of a related character are not normally found in substantial proportions in straight-run petroleum distillates, except in rare instances, nevertheless the trend of the industry towards highly cracked products or "aromatized" stock renders some account of the behavior of at least a few of the lower members of the benzene series an appropriate part of the present text.

Benzene reacts with the halogens either by addition or substitution, but toluene and the higher homologues give substitution products almost exclusively. In the latter case, however, the halogens may enter the side chain or the aromatic nucleus, depending upon conditions. The most important factors influencing the position which the halogens will take are temperature, illumination, catalysts, and to some degree the concentration of the reacting substances. High temperatures and exposure to light promote replacement in the side chain, and low temperatures, absence of light, and the activity of halogen carriers (iodine, iron or aluminum halides) favor nuclear substitution.[1]

CHLORINATION OF BENZENE

Photochemical Chlorination. Smith, Noyes and Hart[2] report that the photochemical chlorination of benzene vapor proceeds by a short chain reaction. There are two simple ways in which the chlorine atoms might substitute in benzene,

$$\begin{aligned} Cl + C_6H_6 &\rightarrow C_6H_5Cl + H && (1)\\ Cl + C_6H_6 &\rightarrow C_6H_5 + HCl && (2) \end{aligned}$$

and these would be followed by either

$$\begin{aligned} H + Cl_2 &\rightarrow HCl + Cl, \text{ or} && (3)\\ C_6H_5 + Cl_2 &\rightarrow C_6H_5Cl + Cl && (4) \end{aligned}$$

Since both addition and substitution occur, according to the investigators, neither reaction 1 nor 2 can be logically excluded, though relatively little can be said concerning their probability. Another mechanism which may be postulated is

$$\begin{aligned} Cl_2 + h\nu &\rightarrow Cl + Cl && (5)\\ Cl + Cl_2 + C_6H_6 &\rightarrow C_6H_6Cl_3 && (6)\\ C_6H_6Cl_3 &\rightarrow C_6H_6Cl_2 + Cl && (7)\\ C_6H_6Cl_3 &\rightarrow C_6H_6 + Cl_2 + Cl && (8)\\ Cl + Cl &\rightarrow Cl_2 && (9) \end{aligned}$$

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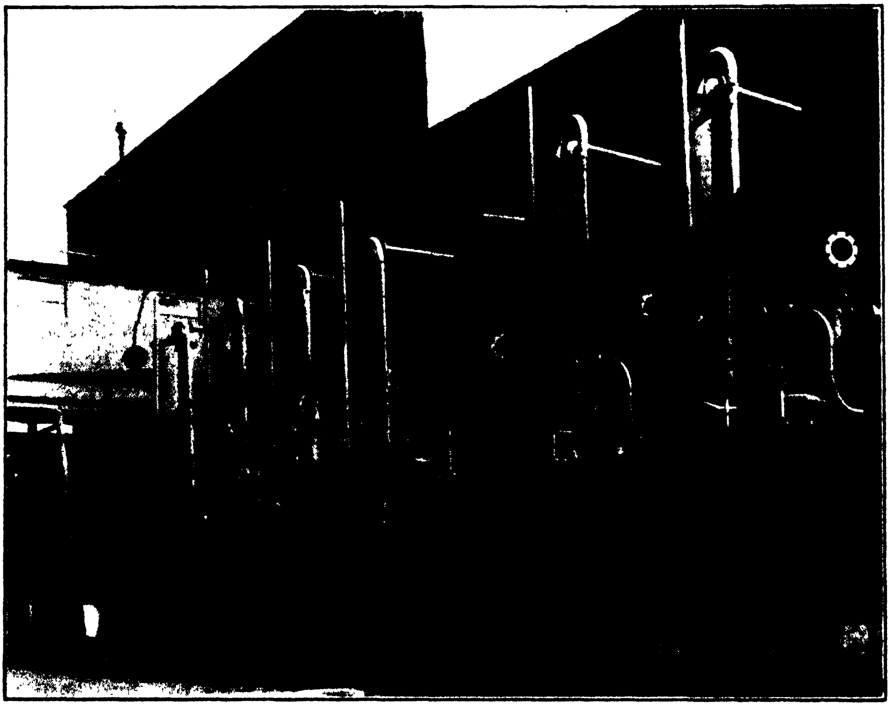
[1] The mechanism of the action of halogen carriers is discussed by Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[2] H. P. Smith, W. A. Noyes, Jr., and E. J. Hart, *J.A.C.S.*, 1933, **55**, 4444; *Chem. Abs.*, 1934, **28**, 709; *Brit. Chem. Abs.* **A**, 1934, 40.

where $h\nu$ = quantum of energy. At the beginning of the reaction, the rate of decrease of pressure is found to be proportional to the square root of the light intensity, and to the separate pressures of the chlorine and benzene.

Luther and Goldberg[3] have stated that oxygen acts as a powerful inhibitor upon the photochemical chlorination of benzene. To overcome this difficulty Nozicka[4] employed anthraquinone together with activated carbon as catalysts in the preparation of chlorobenzene from chlorine and benzene in the presence of light.



Courtesy Dow Chemical Co.

FIG. 169.—Benzene Chlorinators.

Catalytic Chlorination. A chlorination catalyst (halogen carrier) will effect substitution rather than addition in benzene in the absence of light and at ordinary temperatures. For example, a mixture of silicon, antimony trichloride and lead may be employed to secure phenyl chloride.[5] If the chlorination is continued the para isomer will be obtained. With the reactants in the vapor phase and with oxygen present, Mares[6] suggests an aluminum compound with copper, iron or cerium, or, alternatively, a Deacon process catalyst (clay saturated with cupric chloride). The temperature is maintained between 200° and 400°C. Other

[3] R. Luther and E. Goldberg, *Z. physik. Chem.*, 1906, **56**, 43; *J.C.S.*, 1906, **90** (2), 641. See Carleton Ellis, *loc. cit.*

[4] F. Nozicka, U. S. P. 1,945,067, Jan. 30, 1934, to Vereinigte Chemische Fabriken Kreidl, "Heller & Co."; *Chem. Abs.*, 1934, **28**, 2273. Austrian P. 141,082, 1935; *Chem. Abs.*, 1935, **29**, 3916.

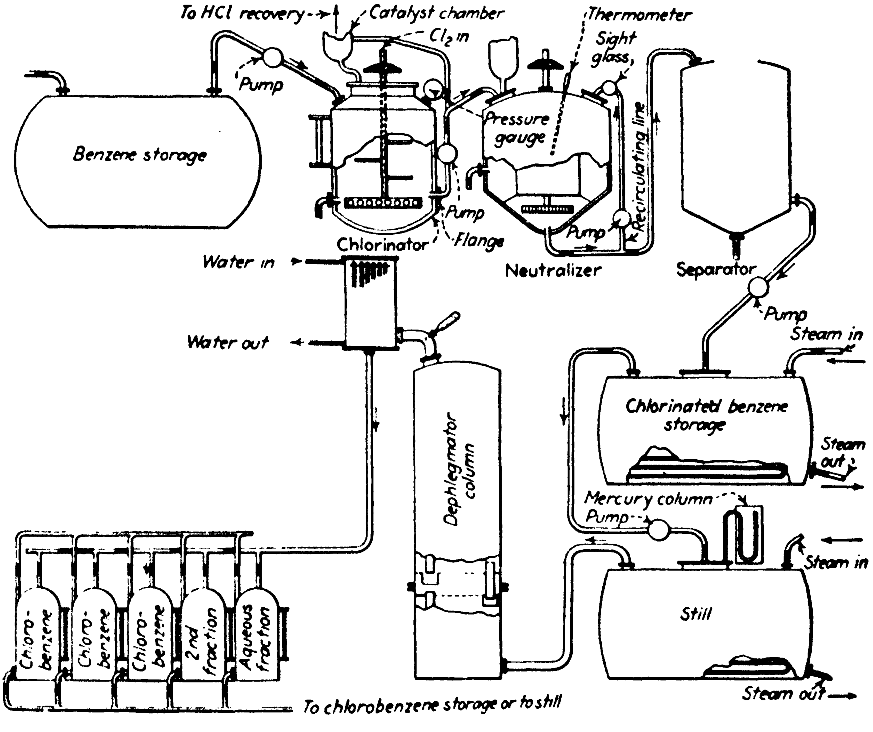
[5] W. C. Stoesser and F. B. Smith, U. S. P. 1,946,040, Feb. 6, 1934, to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1934, 1003; *Chem. Abs.*, 1934, **28**, 2372. Phenyl chloride is, of course, an alternative name for chlorobenzene.

[6] J. R. Mares, U. S. P. 1,935,648, Nov. 21, 1933, to Monsanto Chemical Co.; *Brit. Chem. Abs.* **B**, 1934, 793; *Chem. Abs.*, 1934, **28**, 776.

contact agents include copper with a promoter consisting of cobalt, nickel, manganese or chromium, deposited on pumice or silica gel.[7] According to Likhosherstov and Aldoshin[8] chlorination of benzene with the aid of dichloropentamethylenetetramine and a small proportion of potassium chloride takes place smoothly and may be represented by

$$(CH_2)_5N_4Cl_2 + 2KCl + 2C_6H_6 \longrightarrow 2C_6H_5Cl + 2KCl + (CH_2)_5N_4H_2$$

The procedure consists in dissolving a mixture of benzene and potassium chloride in acetone and adding powdered dichloropentamethylenetetramine in small portions. Since the reaction is exothermic, cooling may be necessary, especially if too great a proportion of the amine is employed. Vorozhtzov, Zilberman and Grigor'ev[9] state that the yield of polychloro derivatives of benzene will be reduced to a minimum if the chlorination is carried out in the liquid phase at 35°C. in a series of columns packed with glass and iron rings. On the other hand Krivonos[10] main-



Courtesy McGraw-Hill Book Co., Inc.

FIG. 170.—Plant Assembly for Chlorination of Benzene. (P. H. Groggins)

tains that continuous stirring will achieve the same results, thus eliminating the necessity for a complicated apparatus.

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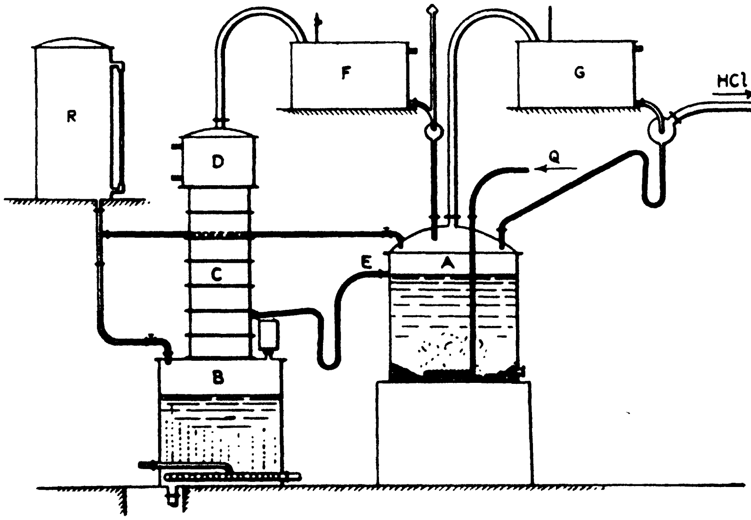
[7] W. Prahl, U. S. P. 1,963,761, June 19, 1934, to F. Raschig G.m.b.H.; *Chem. Abs.*, 1934, **28**, 5080.

[8] M. V. Likhosherstov and T. D. Aldoshin, *J. Gen. Chem.* (*U.S.S.R.*), 1935, 5, 981; *Chem. Abs.*, 1936, **30**, 1033.

[9] N. N. Vorozhtzov, G. B. Zilberman and V. M. Grigor'ev, *J. Applied Chem. (U.S.S.R.)*, 1935, **8**, 872; *Chem. Abs.*, 1936, **30**, 4472; *Brit. Chem. Abs.* **B**, 1935, 1036; *J. Inst. Pet. Tech.*, 1936, **22**, 462A.

[10] F. F. Krivonos, *Ukrain. Khem. Zhur.*, 1935, 10, 417; *Brit. Chem. Abs.* **A**, 1936, 599; *Chem. Abs.*, 1936, **30**, 2932.

Electrolytic Chlorination. Jeunehomme[11] reports that phenyl chloride may be obtained by electrolysis of a solution of benzene, chlorine and hydrogen chloride in methanol. The anode is composed of carbon, the cathode of bright platinum, and the final product other than the halide is hydrogen. In explanation, the same investigator[12] postulates two reactions which occur simultaneously. In one the benzene reacts with dissolved chlorine molecules, and in the other with chlorine atoms on the surface of the anode.



Courtesy McGraw-Hill Book Co., Inc.

FIG. 171.—Equipment for Continuous Chlorination of Benzene. (P. H. Groggins)

A. Chlorinating vessel
B. Heating chamber
C, D. Fractionating column
E. Overflow from chlorination
F. Condenser
G. Scrubber
Q. Chlorine inlet
R. Benzene reservoir

Thermal Chlorination. Space velocity, that is, the number of volumes of gas, at the reaction tube temperature, passing through the heated zone in a definite length of time (usually per minute), influences the thermal chlorination of benzene.[13] For a given space velocity there is a critical temperature below which the amount of chlorine unconsumed increases rapidly. Above a certain temperature pyrolysis sets in and carbon is deposited. In one process a vaporized mixture containing 22.4 per cent of monochlorobenzene and 77.6 per cent of polychlorobenzenes is passed through an electrically heated silica tube at 800°C. and at the rate of 175 g. per hour. Chlorine is introduced at the same time at a velocity of

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[11] W. Jeunehomme, *J. Chim. Phys.*, 1935, **32**, 173; *Brit. Chem. Abs.* **A**, 1935, 709; *Chem. Abs.*, 1935, **29**, 3609.

[12] W. Jeunehomme. *J. Chim. Phys.*, 1935, **32**, 173; *Brit. Chem. Abs.* **A**, 1935, 709; *Chem. Abs.*, 1935, **29**, 3609.

[13] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

9.5 l. per hour.[14] The time of contact is 29.5 seconds and the yield contains 2.8 per cent monochlorobenzene, 87.1 per cent polychlorobenzenes, 8.9 per cent chlorinated biphenyls and 1.2 per cent tarry matter. A method of halogenating benzene with chlorine in the presence of an oxide of zinc, ferric iron or manganese has been proposed.[14a] If the substitution is effected in the absence of water and at 40°C., *p*-dichlorobenzene is reported to be the main product. The advantage of the process is said to be that chlorine monoxide, formed from zinc oxide and chlorine, is the halogenating agent. Thus, the formation of hydrogen chloride is prevented since the products consist of the dichlorobenzene and water.

$$\begin{aligned} 2ZnO + 2Cl_2 &\longrightarrow Zn_2Cl_2O + Cl_2O \\ C_6H_6 + Cl_2O &\longrightarrow C_6H_4Cl_2 + H_2O \end{aligned}$$

Liquid-Phase Chlorination. The substitution of chlorine in benzene with the resulting formation of benzene hexachloride ($C_6H_6Cl_6$)[14b] may be accomplished by mixing the two reactants in an autoclave (Fig. 172) in the liquid phase at a temperature of —15°C. and a pressure of 4 atmospheres.[15] Also, it has been pointed out that benzene hexachloride may be secured from the chlorination of a mixed petroleum-coal distillate.[16] The fraction of the latter mixture which distills in the range 75-90°C. is treated with chlorine in the presence of a layer of water. During the halogenation the reaction vessel is kept in an ice-water bath to control the heat of the reaction.

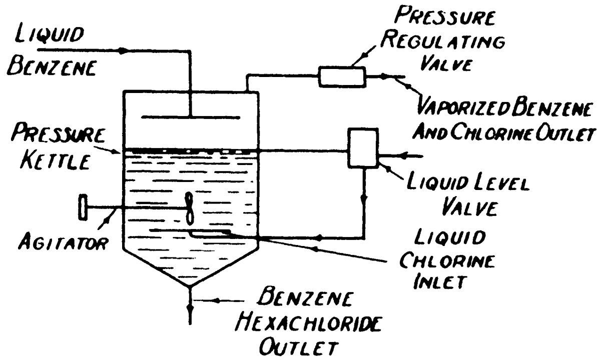
Liquid Benzene
Pressure Kettle
Agitator
Pressure Regulating Valve
Vaporized Benzene And Chlorine Outlet
Liquid Level Valve
Liquid Chlorine Inlet
Benzene Hexachloride Outlet

Fig. 172. Sketch of Method for Hydrocarbon Chlorination with Liquid Chlorine. (H. Bender)

Miscellaneous Chlorination. To prepare 1,2,4,5-tetrachlorobenzene, Mills[17] employs crude *o*-dichlorobenzene containing between 5 and 20 per cent of *p*-dichlorobenzene. The mixture is treated with chlorine at 20-30°C., giving a crystalline product. After filtration, the latter is washed with some of the original halide. Filtrate and washings are recovered and chlorinated to obtain a maximum yield.

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[14] K. S. Jackson, G. E. Wainwright and R. G. Hailes, British P. 436,653, 1935, to Imperial Chemical Industries Ltd.; *J. Inst. Pet. Tech.*, 1935, **21**, 460A.

[14a] W. D. Ramage, U. S. P. 2,046,411, July 7, 1936, to Great Western Electro-Chemical Co.; *Chem. Abs.*, 1936, **30**, 5588.

[14b] This may also be designated hexachlorocyclohexane.

[15] H. Bender, U. S. P. 2,010,841, Aug. 13, 1935, to Great Western Electro-Chemical Co.; *Chem. Abs.*, 1935, **29**, 6607; *Brit. Chem. Abs.* **B**, 1936, 921.

[16] H. P. Stephenson and A. L. Curtis, British P. 447,058, 1936; *Chem. Abs.*, 1936, **30**, 6766.

[17] L. E. Mills, U. S. P. 1,934,675, Nov. 7, 1933, to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1934, 873; *Chem. Abs.*, 1934, **28**, 494.

SEPARATION OF CHLORINE DERIVATIVES OF BENZENE

To separate a mixture of mono- and polychlorobenzenes Buchheim[18] suggests that water be added to the composite to give an azeotropic[19] boiling point of 91°C. On distillation, the phenyl chloride will be found in the distillate and the polychloro compounds in the residue. Bennett[20] reports that sulphonyl chloride will react upon *o*-dichlorobenzene, forming *o*-sulphonylchlorobenzene, but will have no effect upon *p*-dichlorobenzene. Thus it may be employed to separate the ortho from the para compound. Addition of zinc dust during distillation of chlorinated hydrocarbons is said to prevent the formation of hydrogen chloride.[21]

USES OF CHLORINE DERIVATIVES OF BENZENE

Monochlorobenzene and polychlorobenzenes have found industrial application in the manufacture of sulphur black dyes,[22] phenols, *o*-dihydroxybenzene, aromatic amines, diaryl ethers and ketones. The properties of the chloro derivatives make them applicable, in some cases, as liquid dielectrics and transformer oils. Miscellaneous uses include the analysis of graphite greases, the separation of wax from hydrocarbon oil, the removal of carbon deposits from engine parts, dissolving paint and varnish, preserving wood, destroying insects, and as solvents for refrigerants.

PREPARATION OF PHENOLS

The hydrolysis of chlorobenzene by steam with the aid of catalysts has been investigated by various workers. Among the contact agents suggested are the oxides of aluminum, thorium, titanium, zirconium and tungsten as well as silica gel.[22a] Also the use of platinum, silver, copper oxide, copper, cuprous chloride and magnesium oxide has been described.[22b] Prahl[23] recommends iron-free fuller's earth with cuprous chloride as a promoter, the reaction taking place at 300-650°C. Rittler[24] advocates the use of acid-treated bleaching clays, e.g., Tonsil, Frankonite, fuller's earth or bentonite. The apparatus consists of a kettle heated by a steam coil and connected to a column containing the contact agent (see Fig. 173). From the catalyst bed the vapors are conducted to a condensing coil, where the phenol, unreacted monochlorobenzene and hydrogen chloride are condensed and returned to the kettle. The latter contains caustic soda to neutralize the hydrogen chloride.

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[18] K. Buchheim, German P. 616,596, 1935, to Chemische Fabrik von Heyden A.-G.; *Chem. Abs.*, 1936, **30**, 484.

[19] The water and halides, when mixed, have a lower boiling point than when alone. After distillation the two substances may be separated; this is known as azeotropic distillation.

[20] N. Bennett, British P. 440,205, 1934, to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs.* **B**, 1936, 182; *Chem. Abs.*, 1936, **30**, 3835.

[21] N. N. Vorozhtzov, V. M. Grigor'ev and G. B. Zilberman, Russian P. 34,545, 1934; *Chem. Abs.*, 1935, **29**, 2973.

[22] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[22a] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. For a review of some of the literature concerning the preparation of phenol from monochlorobenzene, see N. N. Vorozhtzov, Jr., and A. G. Oshuev, *Anilinokrasochnaya Prom.*, 1933, **3**, 245; *Chem. Abs.*, 1934, **28**, 1027. Also N. N. Vorozhtzov, Jr., *Org. Chem. Ind. (U.S.S.R.)*, 1936, **1**, 675; *Chem. Abs.*, 1937, **31**, 669.

[22b] M. A. Popov and V. A. Popova, *J. Applied Chem. (U.S.S.R.)*, 1936, **9**, 1303; *Brit. Chem. Abs.* **B**, 1936, 970.

[23] W. Prahl, U. S. P. 2,009,023, July 23, 1935, to F. Raschig G.m.b.H.; *Chem. Abs.*, 1935, **29**, 5859. *Cf.* W. Prahl and W. Mathes, U. S. P. 2,035,917, March 31, 1936, to F. Raschig G.m.b.H.; *Chem. Abs.*, 1936, **30**, 3444.

[24] W. Rittler, U. S. P. 1,936,567, Nov. 21, 1933, to Chemische Fabrik von Heyden A.-G.; *Brit. Chem. Abs.* **B**, 1934, 825; *Chem. Abs.*, 1934, **28**, 779. French P. 751,158, 1933; *Chem. Abs.*, 1934, **28**, 1049.

In an analogous process[25] a dilute solution of lime is employed to neutralize hydrochloric acid and a fractionating column is placed between the boiler and catalyst bed, the object being to reflux the phenol and thus prevent its recirculation through the cycle. (See Fig. 174.) Other contact agents include aluminum oxide, cupric phosphate and zinc oxide,[26] Holmes' silica gel[27] (containing 10 per cent of copper),[28] silicon dioxide, magnesium chloride and cuprous chloride,[29] hydrated sodium copper silicate[30] and metallic copper.[31] In conducting the hydrolysis of chlorobenzene with sodium hydroxide at 300-400°C. in iron tubes,[32] the addition of 1 per cent or less of sodium oleate or stearate is said to prevent formation of a scale (Fe_3O_4) which is liable to break off and block the tubes.[33]

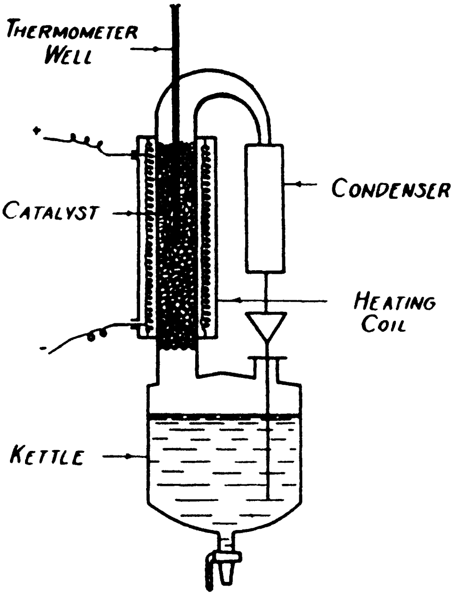

FIG. 173.
Catalytic Hydrolysis of Chlorobenzene to Phenol. (W. Kittler)

While investigating the possibility of preparing *p*-chlorophenol by action of alkalies on *p*-dichlorobenzene, Vorozhtzov and Karlash[34] noticed that phenol appeared as a by-product. It was thought that this reaction was caused by cuprous oxide (formed from metallic copper through the influence of alkalies) and that the reaction was

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[25] R. I. Jenkins and J. F. Norris, U. S. P. 1,950,359, March 6, 1934, to Swann Research, Inc.; *Brit. Chem. Abs.* **B**, 1935, 93; *Chem. Abs.*, 1934, **28**, 3083.

[26] F. A. Steingroever and R. Zellman, U. S. P. 1,961,834, June 5, 1934, to Chemische Fabrik. von Heyden; *Brit. Chem. Abs.* **B**, 1935, 396. *Chem. Abs.*, 1934, **28**, 4745. British P. 404,164, 1933; *Brit. Chem. Abs.* **B**, 1934, 232.

[27] Holmes' silica gel is prepared by adding ferric chloride to a solution of sodium silicate and boiling the gelatinous precipitate with hydrochloric acid. See H. N. Holmes, R. W. Sullivan and N. W. Metcalf, *Ind. Eng. Chem.*, 1926, **18**, 386; *Chem. Abs.*, 1926, **20**, 1694; *Brit. Chem. Abs.* **B**, 1926, 438.

[28] D. Tishchenko and A. M. Churbakov, *J. Applied Chem.* (*U.S.S.R.*), 1934, 7, 764; *Brit. Chem. Abs.* **B**, 1935, 137; *Chem. Abs.*, 1935, **29**, 2520.

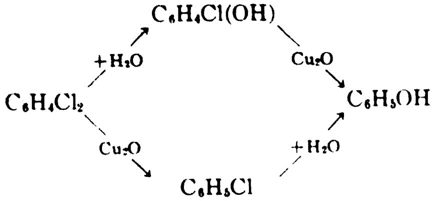
[29] D. Tishchenko, R. Gutner, S. Faerman and M. Shchigelskaya, *J. Applied. Chem.* (*U.S.S.R.*), 1935, **8**, 685; *Chem. Abs.*, 1936, **30**, 4155; *Brit. Chem. Abs.* **B**, 1935, 938. Russian P. 39,114, 1934; *Chem. Abs.*, 1936, **30**, 3441.

[30] J. A. Bertsch, U. S. P. 1,966,281, July 10, 1934, to Monsanto Chemical Co.; *Brit. Chem. Abs.* **B**, 1935, 396; *Chem. Abs.*, 1934, **28**, 5471.

[31] W. J. Hale and E. C. Britton, U. S. P. 1,925,321, Sept. 9, 1933, to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1934, 618; *Chem. Abs.*, 1933, **27**, 5341.

[32] *Cf.* M. E. Putnam, U. S. P. 1,921,373, Aug. 8, 1933, to Dow Chemical Co.; *Chem. Abs.*, 1933, **27**, 5086.

[33] J. J. Crebe and J. H. Reilly, U. S. P. 1,986,194, Jan. 1, 1935, to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1935, 1037, *Chem. Abs.*, 1935, **29**, 1104.



This hypothesis was substantiated when a 50 per cent yield of phenol was obtained by heating *p*-dichlorobenzene with cuprous oxide and water for 3 hours at 275°C.

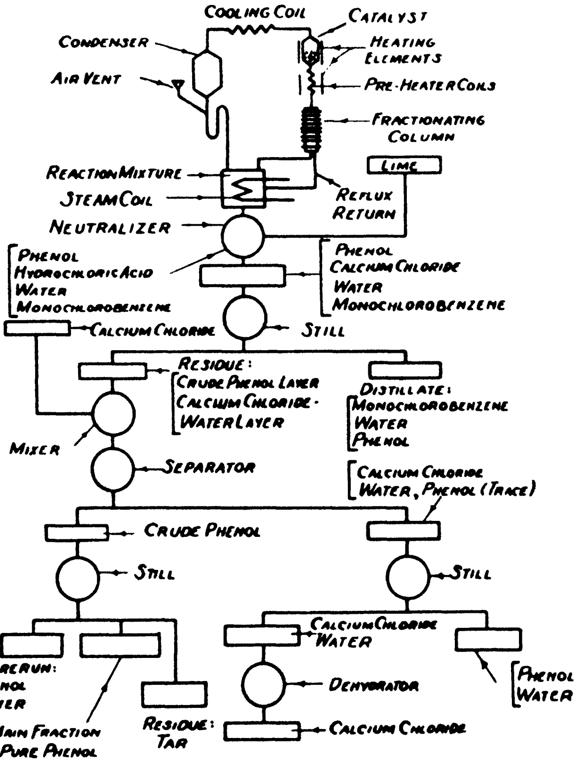


FIG. 174. Flow Chart for Hydrolysis of Chlorobenzene to Phenol. (R. L. Jenkins and J. F. Norris)

and under 80 atmospheres pressure. Similar treatment of *p*-chlorophenol at 250-380°C. also gives phenol.[35]

Preparation of Other Phenolic Substances. Hale[36] reports that the reaction of monochlorobenzene, sodium phenolate and free phenol under pressure at 350-420°C. results in the formation of phenylphenol (hydroxybiphenyl). Heating monochlorobenzene in an aqueous solution of sodium sulphide under pressure at 300°C. furnishes thiophenol.[37]

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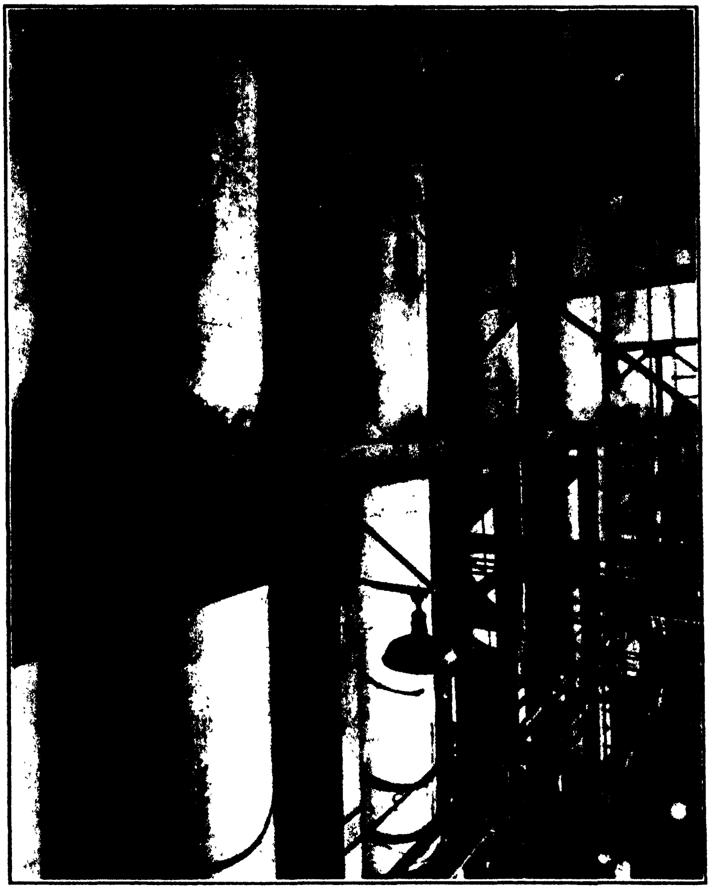
[34] N. N. Vorozhtzov, Jr., and P. V. Karlash, *Compt. rend. acad. sci. U.R.S.S.* (*N.S.*), 1933, 221; *Chem. Abs.*, 1934, 28, 1991; *Brit. Chem. Abs.* A, 1934, 398.

[35] N. N. Vorozhtzov, Jr., and P. V. Karlash, Russian P. 30,689 and 30,690, 1933; *Chem. Abs.*, 1934, 28, 5834.

[36] W. J. Hale, U. S. P. 1,922,695, Aug. 15, 1933, to Dow Chemical Co.; *Brit. Chem. Abs.* B,



Courtesy Dow Chemical Co.

FIG. 175.—View of Synthetic Phenol Plant.

Downing and Clarkson[38] state that the hydrolysis of *o*-dichlorobenzene, employing sodium formate to remove molecular oxygen, leads to *o*-dihydroxybenzene (pyrocatechol). Silver and copper are recommended as contact agents. If some of the reacting material is removed at intervals and allowed to evaporate at atmos-

1934, 536; *Chem. Abs*., 1933, **27**, 5084. A method of purifying phenylphenol with ferric chloride is reported by W. C. Stoesser, U. S. P. 2,050,815, Aug. 11, 1936, to Dow Chemical Co.; *Chem. Abs*., 1936, **30**, 6766.

[37] N. N. Vorozhtzov, Jr., and S. F. Mitzengendler, Russian P. 34,544, 1934; *Chem. Abs*., 1935, **29**, 2977.

[38] F. B. Downing and R. G. Clarkson, U. S. P. 1,969,732, August 14, 1934, to E. I. du Pont de Nemours and Co.; *Chem. Abs*., 1934, **28**, 6160. U. S. P. 1,970,363 and 1,970,364, Aug. 14, 1934. *Brit. Chem. Abs*. **B**, 1935, 716. *Chem. Abs*., 1934, **28**, 6160. British P. 425,230, 1933; *Brit. Chem. Abs*. **B**, 1935, 443; *Chem. Abs*., 1935, **29**, 5458.

pheric pressure, and fresh stock simultaneously added, the process can be made semi-continuous.

PREPARATION OF ANILINE

Vorozhtzov[39] points out that the interaction of monochlorobenzene and aqueous ammonia with a cuprous salt as catalyst proceeds in two steps. In the first the halide reacts with the complex $Cu(NH_3)_2^+$ to form an addition product, according to the equation

$$C_6H_5Cl + Cu(NH_3)_2^+ \longrightarrow C_6H_5Cl \cdot Cu(NH_3)_2^+$$

In this compound the chlorine is very mobile and reacts rapidly with ammonia. yielding phenylamine,

$$C_6H_5Cl{-}{-}Cu(NH_3)_2^+ + NH_3 \longrightarrow C_6H_5NH_2 + HCl + Cu(NH_3)_2^+$$

The velocity of the first step is so much less than that of the second that the former alone determines the overall rate of reaction. The effect is to make the rate of consumption independent of the concentration of ammonia, as represented by

$$\frac{dx}{dt} = K(a-x)b$$

where $\frac{dx}{dt}$ is the rate of increase of product with respect to time, a is the initial concentration of phenyl chloride, x is the concentration of product at time t, b is the concentration of the catalyst and K is the reaction velocity. On the other hand, Groggins and Stirton[39a] maintain that the relation of ammonia concentration to amination and conversion for both catalytic and noncatalytic reactions is significantly altered by changes in temperature and ammonia liquor ratio. Also, they state that while for any particular ammonia concentration the rate of conversion is a function of the copper concentration, the anion accompanying the copper also exerts an influence on the reaction rate. With reference to the type of catalyst employed, Groggins and Stirton hold that:

1. Cupric and cuprous compounds are about equally active in the preparation of amines which are not readily susceptible to oxidation.
2. In the preparation of easily oxidizable amines, such as aniline, a low catalyst concentration results in a smaller difference in the reaction rates when cuprous and cupric compounds are compared.
3. The treatment of aniline with cupric nitrate leads to a much greater oxidation of amine than with cuprous chloride.

Vorozhtzov and Kobelev[40] report that phenylamine may be obtained by heating the corresponding chloride with concentrated ammonium hydroxide and cuprous oxide for two hours at a temperature of 250°C. and a pressure of 70 atmospheres. Hale[41] suggests the addition of some secondary and tertiary amines to the original material. The latter establish an equilibrium with the primary amine, and prevent the formation of more of the secondary and tertiary type. For vapor-phase reaction at 350°C. Prahl and Mathes[42] propose a promoter consisting of phosphoric acid and copper in silica gel. The use of an inorganic oxidizing salt to aid the reaction is recommended by Wuertz.[43] Potassium chlorate, ammonium nitrate and reduced copper may be used at temperatures of 160-220°C.

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[39] N. N. Vorozhtzov, Jr., *Anilinokrasochnaya Prom.*, 1934, 4, 332; *Brit. Chem. Abs.* **B**, 1934, 1002; *Chem. Abs.*, 1935, **29**, 668.

[39a] P. H. Groggins and A. J. Stirton, *Ind. Eng. Chem.*, 1936, **28**, 1051; *Brit. Chem. Abs.* **B**, 1936, 1080; *Chem. Abs.*, 1936, **30**, 7977.

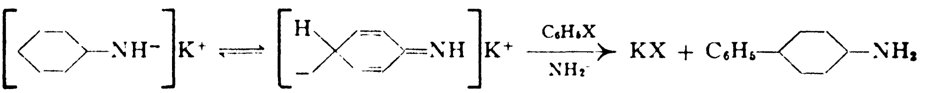
[40] N. N. Vorozhtzov, Jr., and V. A. Kobelev, *J. Gen. Chem.* (*U.S.S.R.*), 1934, 4, 310; *Chem. Abs.*, 1935, **29**, 1787; *Brit. Chem. Abs.* **A**, 1934, 1342.

[41] W. J. Hale, U. S. P. 1,932,518, Oct. 31, 1933, to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1934, 873; *Chem. Abs.*, 1934, **28**, 485.

[42] W. Prahl and W. Mathes, U. S. P. 2,001,284, May 13, 1935, to F. Raschig G.m.b.H.; *Chem. Abs.*, 1935, **29**, 4382; *Brit. Chem. Abs.* **B**, 1936, 921.

The formation of phenylamine from monochlorobenzene has been studied to determine the course of the reaction and the rate of speed of substitution of the chlorine atom as compared to the other halogens.[44] It was stated that liquid ammonia solutions of potassium amide at —33°C. react very readily with monochloro-, monobromo- and monoiodobenzene to give aniline, diphenylamine, small quantities of *p*-aminobiphenyl and traces of triphenylamine. This may be represented as:

$$C_6H_5X + KNH_2 \longrightarrow C_6H_5NH_2 + KX$$
$$C_6H_5NH_2 + KNH_2 \longrightarrow C_6H_5NHK + NH_3$$
$$C_6H_5NH_2 + C_6H_5X \xrightarrow{NH_2^-} (C_6H_5)_2NH + NH_3$$
$$(C_6H_5)_2NH + KNH_2 \longrightarrow (C_6H_5)_2NK + NH_3$$
$$(C_6H_5)_2NK + C_6H_5X \xrightarrow{NH_2^-} (C_6H_5)_3N + KX$$



It was reported that the halogen group is removed almost quantitatively from monochlorobenzene by a liquid ammonia solution of an excess of potassium amide. However, when the halide is present in excess, potassium chloride is formed in yields of 50 to 60 per cent of the theoretical, as calculated from the first equation above. From this it was concluded that the second reaction, in which potassium anilide is produced, is more rapid than the first. Since the yield of halide ion is slightly greater than 50 per cent, calculated from the first and second equations, it was thought that potassium anilide and potassium diphenylamide must further react in the sense of the third, fifth and sixth equations. For these latter reactions the amide ion was said to be necessary as a catalyst.

Competitive experiments in which an ammonia solution of potassium amide was added to an excess of a mixture of aryl halides in the same solvent, indicated that bromine, iodine and chlorine, in that order, are replaced by potassium amide. Fluorine did not react under the conditions of the experiment.

The apparatus in which the reactions were effected consists of two Pyrex cells, both cooled by a liquid-ammonia bath. The cells are connected through a siphon so that solutions may be quantitatively transferred from the first to the second cell (see Fig. 176). Both cells are connected to a waste ammonia line and to a mercury bubbler. The latter is also joined to a gas collector. The potassium amide is incorporated in liquid ammonia in the first cell, and the entire contents are passed to the second reaction vessel. This contains a weighed amount of monochlorobenzene, delivered from a weight pipette.

Preparation of Other Amines. Treatment of 1,2-dichlorobenzene with ammonium hydroxide and reduced copper at a temperature of 150°C. and a pressure of 80 atmospheres will furnish 1,2-diaminobenzene.[45] The purpose of the copper is to form a complex with ammonia, as mentioned previously in the discussion of aniline.

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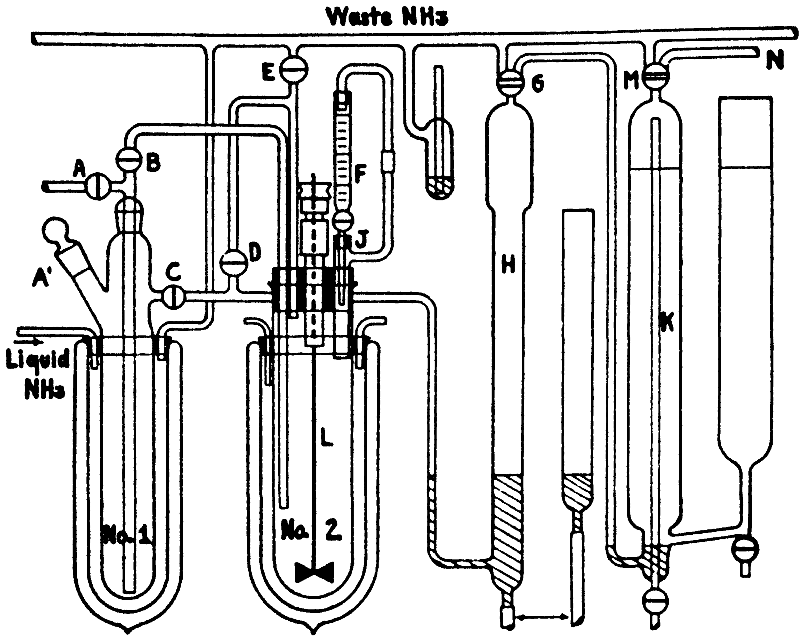
[43] A. J. Wuertz, U. S. P. 1,994,845, March 19, 1935, to E. I. du Pont de Nemours & Co., *Chem. Abs.*, 1935, **29**, 2973. British P. 402,063, 1933; *Chem. Abs.*, 1934, **28**, 3080; *Brit. Chem. Abs.* B, 1934, 186.

[44] F. W. Bergstrom, R. E. Wright, C. Chandler and W. A. Gilkey, *J. Org. Chem.*, 1936, **1**, 170; *Chem. Abs.*, 1936, **30**, 7103. See also, Chapter 34.

[45] Swiss P. 177,262, 1935, to Soc. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1936, **30**, 110. French P. 788,348, 1935; *Chem. Abs.*, 1936, **30**, 1395 C. Graenacher and R. Sallmann, U. S. P. 2,036,134, March 31, 1936, to Soc. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1936, **30**, 3444. French P. 788,348, 1935; *Chem. Abs.*, 1936, **30**, 1395 Swiss P. 177,262, 1935; *Chem. Abs.*, 1936, **30**, 110.



Courtesy Williams and Wilkins Co

FIG. 176.—Apparatus for Reaction of Benzene Halides with Potassium Amide in Liquid Ammonia. (F. W. Bergstrom, R. E. Wright, C. Chandler and W. A. Gilkey)

1, 2. Pyrex cells
A, A'. Source of Ammonia
B. Siphon
C, D. Stopcocks
E. Waste ammonia line
F. Weight pipette
G, M. Three way stopcocks
H. Mercury bubbler
J. Chlorobenzene inlet
K. Gas collector
L. Stirrer
N. Outlet

Vogt[46] states that a phenol such as *m*-cresol may be heated with ammonia and hydrogen under 50-300 atmospheres pressure, employing hydrated alumina as a contact agent to give *m*-toluidine. Horsley[47] suggests ferric chloride as catalyst.

MISCELLANEOUS USES

Osterman[48] reported a method of preparing phenyl ether from phenol, potassium hydroxide and monochlorobenzene. The phenol is first combined with the hydroxide, and deprived of water:

$$C_6H_5OH + KOH \longrightarrow C_6H_5OK + H_2O$$

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[46] E. Vogt, U. S. P. 2,013,873, Sept. 10, 1935, to General Aniline Works; *Chem. Abs.*, 1935, **29**, 6903.

[47] G. F. Horsley, U. S. P. 2,013,052, Sept. 3, 1935, to Imperial Chemical Industries Ltd.; *Chem. Abs.*, 1935, **29**, 6902.

[48] L. Osterman, U. S. P. 1,099,761, June 9, 1914; *Chem. Abs.*, 1914, **8**, 2779.

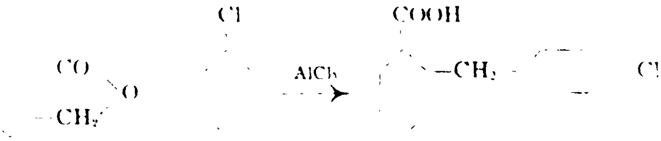
the dry phenolate is dissolved in phenol, mixed with monochlorobenzene and heated to 200-220°C., causing the formation of phenyl ether,

$$C_6H_5OK + C_6H_5Cl \longrightarrow C_6H_5OC_6H_5 + KCl$$

which is expelled from the reaction zone by steam and purified by distillation, the portion boiling at 115-116°C. under 7 mm. pressure being retained. Use of copper as catalyst and employment of temperatures of 300-340°C. have been proposed.[49]

To secure 4-chloroacetophenone, Groggins[50] condensed acetic anhydride with phenyl chloride by the Friedel-Crafts reaction using anhydrous aluminum chloride at a temperature of 100°C. The reaction was effected in a crystallizing pan equipped with a hermetically sealed cover, a modified plow for agitation of the charge, and a side door for discharging the reaction mass.

Jaeger and Daniels[51] point out that the same type of synthesis may be employed to furnish *p*-chlorobenzylbenzoic acid. The reactants are phthalide and chlorobenzene with anhydrous aluminum chloride, and their combination may be represented by



Clark[52] reports that some chlorohydrocarbons, particularly pentachlorobiphenyl and trichlorobenzene, are capable of serving as liquid dielectrics (e.g., as transformer oil). These are said to be oil-insoluble, stable, neutral and non-volatile. A mixture of the isomers of pentachlorobiphenyl has a pour point of 10°C. with no crystal formation, and a dielectric constant[53] of 5 at 25°C. The relatively high pour point of pentachlorobiphenyl would limit its use were it not for the fact that when mixed with trichlorobenzene it forms a composite having a pour point of —18°C. Although the latter is combustible under flash-producing conditions, it is said that the addition of 10 per cent of ethylene chloride will eliminate this undesirable property.[54]

In the analysis of commercial greases which contain graphite, it is often a matter of difficulty to separate such ether-insoluble materials as calcium stearate. Biffen[55] has proposed trichlorobenzene for this purpose; it is heated with the grease to 165°C., centrifuged and the halide decanted. Similarly a mixture of *o*-dichlorobenzene and either ethylene glycol or amyl alcohol is employed by McCarty and Skelton.[56]

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[49] K. Marx and H. Wesche, U. S. P. 2,008,987, July 23, 1935, to Winthrop Chemical Co.; *Chem. Abs.*, 1935, **29**, 5856. See also French P. 755,051, 1933, to I. G. Farbenind. A.-G., *Chem. Abs.*, 1934, **28**, 1365. N. N. Vorozhtzov, Jr., and A. G. Oshuev, Russian P. 40,345, 1934; *Chem. Abs.*, 1936, **30**, 3838.

[50] P. H. Groggins, U. S. P. 1,991,743, Feb. 19, 1935, to the Secretary of Agriculture U. S. A.; *Chem. Abs.*, 1935, **29**, 2175. U. S. P. 2,008,418, July 16, 1935; *Chem. Abs.*, 1935, **29**, 5856.

[51] A. O. Jaeger and L. C. Daniels, U. S. P. 1,981,360, Nov. 20, 1934, to American Cyanamid and Chemical Corp.; *Chem. Abs.*, 1935, **29**, 479; *Brit. Chem. Abs.* **B**, 1935, 940.

[52] F. M. Clark, *Chem. Trade J.*, 1934, **94**, 329; *J. Inst. Pet. Tech.*, 1934, **20**, 382A. U. S. P. 1,944,730, Jan. 23, 1934, to General Electric Co.; *Brit. Chem. Abs.* **B**, 1935, 193; *Chem. Abs.*, 1934, **28**, 2082. British P. 430,045, 1934, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs.* **B**, 1935, 773; *Chem. Abs.*, 1935, **29**, 8177. *Cf.* R. Freitag and H. A. Lühl, *Maschinenschaden*, 1934, **11**, 160; *Chem. Zentr.*, 1935, I, 338; *Brit. Chem. Abs.* **B**, 1935, 661.

[53] Dielectric constant is defined by D in the equation $F = \frac{qq'}{Dd^2}$ where F is the force between two charged points, q and q' are the charges on these points and d is the distance between the two points.

[54] F. M. Clark, U. S. P. 2,019,339, Oct. 29, 1935, to General Electric Co.; *Chem. Abs.*, 1936, **30**, 282.

[55] F. M. Biffen, *Ind. Eng. Chem. Anal. Ed.*, 1934, **6**, 169; *Chem. Abs.*, 1934, **28**, 4892; *Brit. Chem. Abs.* **B**, 1934, 634.

[56] B. Y. McCarty and W. E. Skelton, U. S. P. 2,035,490 and 2,035,491, March 31, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 216A; *Chem. Abs.*, 1936, **30**, 3630.

Incorporation of 2 per cent of *o*-dichlorobenzene to mineral oil lubricants is said to reduce friction.[57]

Gerlach[58] recommends *o*-dichlorobenzene for removing carbon deposits from engine valves or pistons. The halide is mixed with triethanolamine and oleic acid and heated, with water, to 150-200°C. to form the cleaning bath. When mixed with kerosene and red oil, the dihalide is suggested as a cleansing agent for the water-circulating systems of automobiles.[59]

To secure a paint and varnish remover, propene dichloride and *o*-dichlorobenzene may be added to a lesser volume of acetone, carbon tetrachloride and benzene.[60]

Calcott and Foreman[61] use a 5 per cent solution of nitronaphthalene in *o*-dichlorobenzene to protect wood from fungus growth. The halide is employed as a solvent for methyl chloride in one absorption-type refrigerating apparatus.[62]

Both *o*- and *p*-dichlorobenzene have been suggested as insecticidal compositions. With the former, a mixture of the dihalide, ethyl alcohol, β-naphthol, rosin and a volatile petroleum solvent is used in termite control.[62a] In the extermination of moths, *p*-dichlorobenzene is said to be effective.[62b]

As a lubricant, a mixture of a lubricating oil and 1,2,4-trichlorobenzene has been proposed.[62c]

BROMINATION OF BENZENE

The bromination of benzene has not been reported in detail, but it would seem, in general, to resemble the chlorination of that hydrocarbon. Photochemical reaction using dry reagents results in addition products, while halogen carriers promote substitution.[63]

The activity of selenium and tellurium as carriers has been studied and contrasted with that of iron by O'Kelly.[64] In the reaction flask were placed 70.3 g. of benzene, 2 g. of iron and 0.5 g. of anhydrous aluminum chloride. Bromine was added until an excess of 80 per cent was present, and the mixture allowed to stand 12 hours at room temperature and an additional 7 hours with slight heating. Selenium, tellurium and a mixture of tellurium and iron were substituted singly in each of the succeeding runs. Results of the investigator have been compiled in Table 158.

Employment of such carriers as sulphur, iodine, antimony, bismuth and mercury in association with sulphonyl chloride with which the carriers are capable of oxidizing hydrogen bromide, has been proposed.[65] Normal temperatures and the

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[57] C. F. Prutton, U. S. P. 1,986,645 and 1,986,651, Jan. 1, 1935, to Lubri-Zol Corp.; *Brit. Chem Abs.* **B**, 1935, 1128; *Chem. Abs.*, 1935, **29**, 1242. *Cf.* D. S. Velikovskii, Russian P 41,103, 1935; *Chem. Abs.*, 1936, **30**, 7324.

[58] R. G. Gerlach, U. S. P. 2,006,636, July 2, 1935; *Chem. Abs.*, 1935, **29**, 5634; *Brit. Chem. Abs.* **B**, 1936, 628.

[59] F. Amthor and G. C. Reinhard, U. S. P. 2,036,848, April 7, 1936, to American Colloid Co; *Chem. Abs.*, 1936, **30**, 3548.

[60] L. E. Mills and S. W. Putnam, U. S. P. 1,938,714, Dec. 12, 1933, to Dow Chemical Co; *Brit. Chem. Abs.* **B**, 1934, 896; *Chem. Abs.*, 1934, **28**, 1488.

[61] W. S. Calcott and M. O. Foreman, Canadian P. 343,744, 1934, to The Canadian Industries Ltd.; *Chem. Abs.*, 1934, **28**, 7466. *Cf.* L. E. Mills, U. S. P. 2,017,506, Oct. 15, 1935; *Chem. Abs.*, 1935, **29**, 8220. G. Algard, British P. 440,563, 1936; *Chem. Abs.*, 1936, **30**, 3936.

[62] G. F. Zellhoefer, U. S. P. 2,031,087, Feb. 18, 1936; *Chem. Abs.*, 1936, **30**, 2056.

[62a] F. H. Lyons, U. S. P. 2,059,125, Oct. 27, 1936, to E. L. Bruce Co.; *Chem. Abs.*, 1937, **31**, 190.

[62b] Weigelt, *Seifensieder-Ztg.*, 1936, **63**, 608; *Chem. Abs.*, 1936, **30**, 7247.

[62c] C. F. Prutton and A. K. Smith, British P. 453,114, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 512A; *Chem. Abs.*, 1937, **31**, 1607.

[63] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

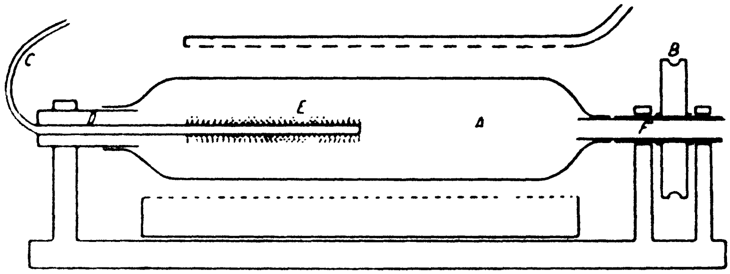
[64] A. A. O'Kelly, *J.A.C.S.*, 1934, **56**, 2783; *Chem. Abs.*, 1935, **29**, 747; *Brit. Chem. Abs.* **A**, 1935, 203.

[65] M. A. Kunz, K. Köberle and E. Berthold, German P. 595,461, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 4066.

TABLE 158.—*Comparison of Degree of Bromination of Benzene in Presence of Various Halogen Carriers.*

Carrier	Benzene Grams	Monobromobenzene Grams	Yield %	Dibromobenzene Grams	Yield %
Iron	70.3	65.6	46.2	10	4.6
Selenium	70.3	36.0	25.4	7	3.2
Tellurium	70.3	43.5	30.7	15	6.9
Tellurium-Iron	70.3	65.6	46.2	10	4.6

absence of light are utilized in the process, and tetra-, penta- and hexabromobenzenes are formed. Ferric chloride hexahydrate ($FeCl_3-6H_2O$), according to Menke,[66] or ferrous sulphate heptahydrate ($FeSO_4-7H_2O$) as well as the anhydrous salts are aids in the bromination of benzene. Addition of a nitrate or nitrite inhibits the activity of the catalysts. The employment of beryllium bromide as a catalyst for the bromination of benzene has been suggested.[67] With the reactants at 20°C., the products are said to contain mono-, di- and tribromobenzene.



Courtesy Deutsche Chemische Gesellschaft
Courtesy Verlag Chemie G.m.b.H.

FIG. 177.—Rotatable Cylinder Employed for Fluorination of Benzene. (K. Fredenhagen and G. Cadenbach)

A. Glass tube
B. Guide
C. Copper capillary tube
D. Copper tube
E. Nozzle
F. Shaft

FLUORINATION OF BENZENE

Fredenhagen and Cadenbach[68] have described a device which insures good distribution of fluorine in treating organic substances. It consists of a glass cylinder (externally cooled) which can be rotated about a horizontal axis. A copper tube with numerous fine openings along its length serves to introduce the fluorine. The latter is admixed with 15 volumes of nitrogen to serve as a diluent and to avoid inflammation. Interaction is enhanced by wrapping the tube in copper, silver or iron gauze. At 0°C., treatment of benzene furnished a product which contained 20 per cent of fluorine. Employment of fluorinated hydrocarbons, or other liquids

[66] J. B. Menke, *Chem. Weekblad*, 1934, **31**, 344; *Brit. Chem. Abs.* **A**, 1934, 877; *Chem. Abs.*, 1934, **28**, 6121.

[67] M. F. Taboury and R. Pajeau, *Compt. rend.*, 1936, **202**, 328; *Chem. Abs.*, 1936, **30**, 2836; *Brit. Chem. Abs.* **A**, 1936, 461. R. Pajeau, *Compt. rend.*, 1936, **202**, 1795; *Brit. Chem. Abs.* **A**, 1936, 976; *Chem. Abs.*, 1936, **30**, 5949.

[68] K. Fredenhagen and G. Cadenbach, *Ber.*, 1934, **67**, 928; *Chem. Abs.*, 1934, **28**, 4710; *Brit. Chem. Abs.* **A**, 1934, 878.

inert to fluorine, as diluents in this type of reaction has been proposed.[69] For example, the compound to be treated may be dissolved in liquid hydrogen fluoride, dichlorodifluoromethane, hexafluoroethane or trichlorotrifluoroethane and a catalyst such as iodine or antimony pentachloride added. In one example, 5 g. of benzene was admixed with 71 g. of anhydrous hydrogen fluoride in a copper vessel with an inlet tube of copper extending below the surface of the liquid (see Fig. 178). The reaction vessel was connected to a reflux condenser maintained at a temperature of —70°C. Fluorine was then conducted into the inlet tube until 5 g. had been absorbed. Hydrogen fluoride was then vaporized and the residue neutralized and extracted. In this manner a product containing 45 per cent of fluorine by weight was said to be secured.

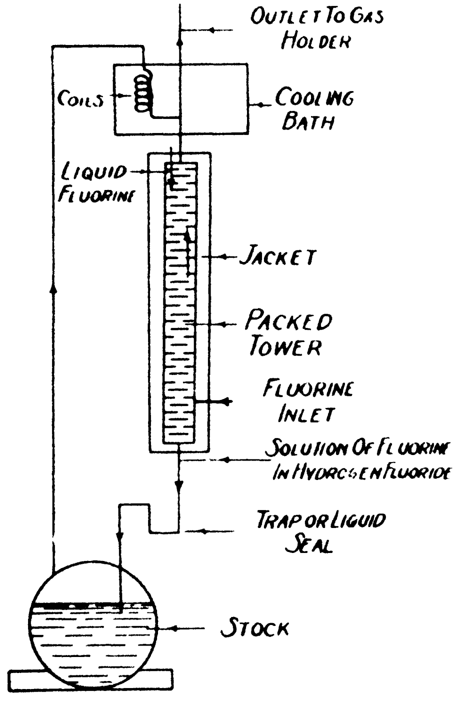


FIG. 178
Employment of Fluorine-containing Diluents in Fluorination of Organic Compounds. (E. I. du Pont de Nemours & Co.)

The fluorination of the chloro derivatives of benzene has received some attention. Daudt and Parmelee[70] point out that fluorochlorobenzenes may be procured by introducing fluorine above the surface of *o*-dichlorobenzene dissolved in trifluorotrichlorobenzene at —25°C. Bigelow and Pearson[71] report that the fluorination of hexachlorobenzene at 0°C. yields principally tetrafluorohexachlorocyclohexene ($C_6Cl_6F_4$, m.p. 113-114°C.) and some hexafluorohexachlorocyclohexane ($C_6Cl_6F_6$, m.p. 94-96°C.).

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[69] British P. 429,591, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 715; *Chem. Abs.*, 1935, **29**, 6901. French P. 761,946, 1934; *Chem. Abs.*, 1934, **28**, 4430.

[70] H. W. Daudt and H. M. Parmelee, U. S. P. 2,013,035, Sept. 3, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 6900.

[71] L. A. Bigelow and J. H. Pearson, *J.A.C.S.*, 1934, **56**, 2773; *Chem. Abs.*, 1935, **29**, 747; *Brit. Chem. Abs.* **A**, 1935, 203.

CHLORINATION OF TOLUENE

It was mentioned in the beginning of this chapter that toluene and its homologues undergo two types of substitution, nuclear and side chain. The factors influencing each substitution were also touched upon, and the conclusion stated that direct chlorination in the sunlight and at high temperatures promotes side chain reaction, while halogen carriers favor nuclear replacement.

Firth and Smith[72] have studied the chlorination of toluene and the effect of two catalysts upon the identity of the resulting halides. The contact agents employed were (a) activated charcoal and (b) iron-impregnated silica gel. The investigators point out that the former accelerates reaction and increases the amounts of side-chain substituents, and the latter induces nuclear substitution and condensation. Light was excluded and the temperature maintained at 110°C. throughout the chlorination. One hundred grams of toluene were employed in each run, and the results are shown in Table 159.

TABLE 159. *Effect of Catalysts on the Chlorination of Toluene*

Series (a) Activated Charcoals

				Yield				
Catalyst and Temp of Activation	Hours of Chlorination	Weight Grams	Density	Benzyl Chloride %	Chlorotoluenes %	Toluene %	Benzaldehyde %	Benzoic Acid Grams
Nil	8	76	1.050	42	37	21	—	—
1 g. sugar charcoal, 600°C.	8	82	1.087	73	24	3	—	—
1 g. sugar charcoal, iodized 600°C.	8	87	1.085	90	8	2	—	—
1 g. sugar charcoal, 900°C	8	61	1.082	89	5	6	-	—
1 g. sugar charcoal, iodized, 900°C.	8	80.5	1.081	88.5	4.5	7	-	—
Blood charcoal, 600°C.	8			—				126
Blood charcoal	4	9.0	1.068	87	3	8	2	Nil
Blood charcoal, 800°C.	8	35.5	1.077	30	7	7	56	32
Blood charcoal, 900°C.	8	70	1.074	68	22	10		Nil
Blood charcoal, 600°C.	16		-		-			33
Artificial blood charcoal, 600°C.	8	98	1.086	81	11	8	—	Nil

Series (b) Iron-Impregnated Silica Gel

Catalyst and Temp of Activation	Hours of Chlorination	Weight Grams	Density	Benzyl Chloride %	Chlorotoluenes %	Toluene %	Benzaldehyde %	Benzoic Acid Grams
1 g. 600°C. for 2 hours	4	64	0.998	Trace	63	37		—
1 g. 120° C. for 12 hours	4	64	1.053	Nil	89	11		—
1 g. 600°C. for 2 hours.	8	49	1.035	19.5	61	19.5	-	-
2 g. 600°C. for 2 hours. .	8			(Crude product, black brittle solid)				

Nikolyuk[73] reports that if toluene is chlorinated in an iron apparatus with a chemically pure lead lining, the yield of benzyl chloride is 15.5 per cent (6.5 to 9.5 per cent over that obtained in glass-lined chambers). Commercial lead, on the other hand, brings about substitution primarily in the nucleus; even upon repeated chlorination the amount of benzyl chloride is small. Lead which has been used in a previous process is more active than that which is being used for the first time, but pretreatment with hydrochloric acid renders the lead less effective. Sulphur increases the amount of products obtained and partially prevents replacement in the nucleus. Alekseevskii and Krasavin[74] state that if a mixture of toluene, chlorine and hydrogen chloride is adsorbed by birch carbon or silicon dioxide and desorbed by steam at 120°C., mono- and dichlorotoluenes result. If aluminum oxide is present, trichlorotoluenes are predominant at the end of reaction.

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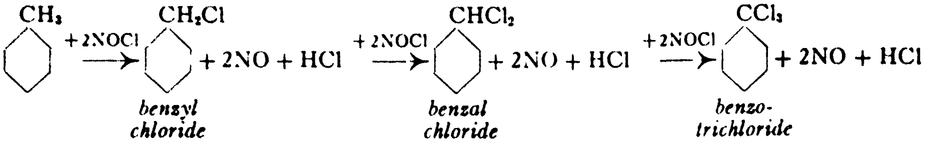
[72] J. B. Firth and T. A. Smith, *J.C.S.*, **1936**, 337; *Brit. Chem. Abs.* **A**, 1936, 599; *Chem. Abs.*, **1936**, **30**, 3790.

[73] B. A. Nikolyuk, *J. Applied Chem. U.S.S.R.*, 1934, 7, 564; *Brit. Chem. Abs.* **B**, 1935, 12; *Chem. Abs.*, **1935**, **29**, 1786. Russian P. 32,491, 1933; *Chem. Abs.*, 1934, **28**, 3422. See also, Z. N. Suirkin and E. E. Pugachev, *Anilinokrasochnaya Prom.*, 1935, 5, 162; *Chem. Abs.*, 1936, **30**, 7528.

[74] E. V. Alekseevskii and S. F. Krasavin, *J. Chem. Ind.* (*Moscow*), 1935, **12**, 838; *Brit. Chem. Abs.* **B**, 1936, 54.

The action of nitrosyl chloride upon toluene has been investigated by Perrot[75] who points out that 2 moles of the halide unite with one of the hydrocarbon at 150°C. in sealed tubes to give benzyl chloride, benzal chloride and benzotrichloride.



The Uses of Chlorine Derivatives of Toluene

Benzyl chloride, like monochlorobenzene, may be hydrolyzed to yield phenolic compounds. For example, Hale[76] recommends that monochlorotoluene be heated in water to 300°C. with ammonia, cuprous oxide and calcium hydroxide to form a mixture of *o*- and *p*-cresol. According to Britton[77] no contact agent is needed for such a reaction if sodium rather than calcium hydroxide is employed. The interaction of higher chlorotoluenes with alcoholic potassium hydroxide at 140-210°C. may be utilized to produce chlorocresols.[78] However, Yamasaki and Titani[79] report that when the benzyl chloride is maintained in the vapor phase, it will not hydrolyze with water vapor after 5 hours heating at 130-200°C. nor with ethyl acetate after 150 hours at the same temperature.

Benzyl chloride may be heated with sodium acetate and acetic acid[80] or with acetic anhydride and bismuth oxide[81] to obtain benzyl acetate. Treatment of benzal chloride with aqueous sodium sulphite is said to result in the formation of benzaldehyde.[82] Also, it has been pointed out that the interaction of benzal chloride with dimethyl ether at 330°C. in the presence of alumina leads to benzene and methyl chloride.[82a] Benzotrichloride, according to Kranzlein and Hopff,[83] can be used in the preparation of naphthalene sulphonyl chloride. The method consists in heating the sodium salt of β-naphthalenesulphonic acid with the trichloride at 150-250°C. Kyrides[84] suggests that benzotrichloride be treated with phthalic anhydride at 200°C. to furnish phthalyl chloride. Zinc chloride may be employed as catalyst.

Cole[85] states that benzyl chloride, incorporated in a high-boiling distillate fraction of coal tar, serves as a corrosion inhibitor for metal surfaces.

Bromination of Toluene

The bromination of toluene is affected to a marked degree by the conditions of the reaction.[86] Temperature and light are two of the important factors in de-

[75] R. Perrot, *Compt. rend.*, 1934, **198**, 1424; *Brit. Chem. Abs.* **A**, 1934, 641; *Chem. Abs.*, 1934, **28**, 4391.

[76] W. J. Hale, U. S. P. 2,028,065, Jan. 14, 1936, to Dow Chemical Co; *Chem. Abs.*, 1936, **30**, 1395.

[77] E. C. Britton, U. S. P. 1,996,744, April 9, 1935, to Dow Chemical Co; *Chem. Abs.*, 1935, **29**, 3354.

[78] C. Jacobi and B. Wolf, U. S. P. 1,995,568, March 26, 1935, to I. G. Farbenind. A G.; *Chem. Abs.*, 1935, **29**, 2976.

[79] S. Yamasaki and T. Titani, *Bull. Chem. Soc. Japan*, 1934, **9**, 501; *Brit. Chem. Abs.* **A**, 1935, 172; *Chem. Abs.*, 1935, **29**, 1311.

[80] F. W. Klever, British P. 20,504, 1913; *Chem. Abs.*, 1915, **9**, 694, *J S.C I.*, 1914, **33**, 375

[81] Swiss P. 169,040, 1934, to L. Givaudan & Cie. Soc. anon; *Chem. Abs.*, 1935, **29**, 481

[82] M. P. Ger, Russian P. 40,349, 1934; *Chem. Abs.*, 1936, **30**, 3838.

[82a] L. Andrussow, German P. 634,549, 1936, to I. G. Farbenind A.-G.; *Chem. Abs.*, 1937, **31**, 419. British P. 452,934, 1936; *Chem. Abs.*, 1937, **31**, 1042.

[83] G. Kranzlein and H. Hopff, U. S. P. 2,016,784, Oct 8, 1935, to I. G. Farbenind. A. G.; *Chem. Abs.*, 1935, **29**, 8005.

[84] L. P. Kyrides, U. S. P. 1,963,749, June 19, 1934, to Monsanto Chemical Co.; *Chem. Abs.*, 1934, **28**, 5079. British P. 414,570, 1934; *Chem. Abs.*, 1935, **29**, 478; *Brit. Chem. Abs.* **B**, 1934, 875.

[85] P. J. Cole, U. S. P. 2,037,762, April 21, 1936, to Barrett Co.; *Chem. Abs.*, 1936, **30**, 3768.

[86] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

termining the position of bromine in the resulting compound. If the halogen is added to cold toluene in the dark, the yield is mainly *o*- and *p*-bromotoluene. At a temperature of 100°C., however, in the absence of light-benzyl bromide is formed exclusively. Thus an increase in temperature favors side-chain substitution. In the presence of diffused daylight at 25°C., benzyl bromide is obtained and no nuclear substitution takes place. This would seem to indicate that the photochemical reaction has a greater effect on the position of bromine than the thermal reaction, provided the same temperature is employed in each case.

Nuclear substitution can be achieved by the activity of halogen carriers such as iodine, iron, antimony and aluminum bromides. In the presence of these substances, an excess of bromine furnishes polybromo derivatives. It is interesting to note that phosphorus pentabromide, unlike the other halides, favors side-chain rather than nuclear substitution.

The bromination of *o*-, *m*- and *p*-chlorotoluenes has been studied by Varma and Sahay.[87] Some of the results of their work are contained in Table 160.

TABLE 160.—*Bromination of Chlorotoluene.*

Chloride	Product	Boiling Point of Product
o-Chlorotoluene	2-Chloro-5-bromotoluene	90-3°C. (12 mm.)
m-Chlorotoluene	3-Chloro-4-bromotoluene 3-Chloro-6-bromotoluene	90-3°C. (12 mm.) 120-5°C. (15 mm.)
p-Chlorotoluene	*p*-Chlorobenzalbromide	

The halogenation of the higher homologues of benzene can occur in two ways, as in the case of toluene and benzene. Nuclear substitution may be brought about in the dark and at low temperatures, and by the use of halogen carriers. In the presence of actinic light or at high temperatures side-chain substitution takes place.

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[87] P. S. Varma and V. Sahay. *J. Indian Chem. Soc.*, 1934, 11, 293; *Chem. Abs.*, 1934, **28**, 5049; *Brit. Chem. Abs.* **A**, 1934, 762.

Chapter 33

Production of Alcohols by Hydrolysis of Alkyl Halides. Production of Esters

The alkyl halides, particularly the bromides and chlorides, are available for the manufacture of alcohols of the aliphatic series. Primary as well as secondary and tertiary alcohols may be prepared by the hydrolysis of the corresponding alkyl halide, distinguishing this process from the hydration of olefins, which yields only secondary and tertiary alcohols (ethanol, of course, being an exception).[1]

The hydrolysis of alkyl halides may be represented by the equation

$$C_nH_{(2n+1)}X \; + \; H_2O \;\rightleftharpoons\; C_nH_{(2n+1)}OH \; + \; HX$$

where X is a halogen but, in general, the point of equilibrium appears to rest on the left side, even at elevated temperatures. For this reason water alone (as liquid or vapor) is seldom used. Instead an alkali such as aqueous caustic soda, milk of lime or aqueous sodium carbonate is employed. The reaction is

$$C_nH_{(2n+1)}X \; + \; M'OH \;\rightleftharpoons\; C_nH_{(2n+1)}OH \; + \; M'X$$

where M′ is one atomic proportion of a monovalent element (or one-half atomic proportion of a divalent element).

Conversion of Methyl Chloride into Methanol

Methyl chloride can be converted to methanol in the liquid phase by using a solvent or in the vapor phase by passing the alkyl halide vapor and steam over heated solid hydroxides and condensing the alcohol vapors formed.[1a] Conducting the halide over calcium hydroxide, aluminum oxide or potassium hydroxide and at temperatures ranging from 300° to 350°C. has been suggested.[2]

Abkin and Medvedev[3] report the use of stannous phosphate deposited on pumice as a catalyst for vapor-phase hydrolysis of methyl chloride. At a temperature of 460°C. and with the ratio of steam to halide 10:1 (by volume) a 16 per cent yield of methanol was obtained. In the liquid phase the chloride may be heated in contact with aqueous alkaline solutions at temperatures of 150° to 190°C. and a pressure of 260 pounds per square inch. Dimethyl ether is also a product of the above reaction. To transform the ether to the alcohol, water and aluminum oxide may be added and the temperature maintained at 350°C.

$$(CH_3)_2O \; + \; H_2O \;\rightleftharpoons\; 2CH_3OH \quad -3 \text{ kg. cal.}^{3a}$$

Conversion of Halides of Ethane to Alcohols

Ethyl chloride reacts with the alkaline hydroxides, oxides and steam in a manner analogous to that for methyl chloride, forming ethanol. In the liquid phase, employment of aqueous potash or caustic soda and temperatures of 250-450°C. is recommended. In the vapor phase at 250°C. the use of a contact agent such as active charcoal impregnated with zinc sulphate is suggested. Diethyl ether is a by-product of both methods. To inhibit ether formation, Hale[4] suggests that

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[1] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[1a] *Cf.* Chapter 29.

[2] Carleton Ellis, *loc. cit.*

[3] A. Abkin and S. Medvedev, *J. Chem. Ind. (Moscow)*, 1934, 10, No. 1, 30; *Brit. Chem. Abs.* B, 1934, 616. *Chem. Abs.*, 1934, 28, 3051. Russian P. 34,551, 1934; *Chem. Abs.*, 1935, 29, 2973.

[3a] Carleton Ellis, *loc. cit.*, 783.

$$3C_2H_5Cl + 3NaOH \rightleftharpoons C_2H_5OH + (C_2H_5)_2O + 3NaCl + H_2O$$

a small proportion of the ether be added to establish an equilibrium with that secured from hydrolysis.

Klebanskii and Dolgopol'skii[5] point out that ethylene glycol $(CH_2OH)_2$ may be obtained by saponifying dichloroethane with sodium carbonate. When a mixture of 200 grams of the halide and 220 grams of the carbonate was heated to 175-195°C. at a pressure of 100 atmospheres, an 87-90 per cent yield of glycol resulted.

HYDROLYSIS OF HIGHER ALKYL HALIDES TO ALCOHOLS

Propyl Chloride. The hydrolysis of propyl halides has apparently received little attention. The work of Hughes[6] indicates that the conversion of isopropyl chloride to the corresponding alcohol (by treatment at 45°C. in 60 per cent of alcohol) is a unimolecular mechanism depending upon the ionization of the alkyl halide.

$$(CH_3)_2CHCl \rightleftharpoons (CH_3)_2CH^+ + Cl^- \text{ followed by}$$
$$(CH_3)_2CH^+ + OH^- \rightleftharpoons (CH_3)_2CHOH \text{ (instantaneously)}$$

The velocity constant[6a] of the reaction in a slightly alkaline medium is 2.60 and in an acid medium 2.58.

Butyl Chloride. Clarke and Cook[7] employ *n*-butyl chloride in preparing butyl alcohol. The halide is mixed with an aqueous suspension of ferrous hydroxide and the composite placed in an autoclave. A temperature of 75-150°C. and a pressure of 300 pounds per square inch are maintained for a period of 4 hours. The amount of alcohol may be increased by having present 1-2 per cent of pyrogallol (a reducing agent),[7a] which prevents the formation of aldehydes and acids.

Sparks and Nelson[8] report that the hydrolysis of 1,2-dichloro-2-methylpropane in the liquid phase at 70-80°C. leads mainly to 1-chloro-2-methyl-2-propanol, under neutral, slightly basic or slightly acidic conditions. The addition of basic substances to the hydrolysis mixtures tends to decrease the amount of alcohol furnished. Some of the results are shown in Table 161.

Saponification of 1,2,3-trichloro-2-methylpropane in dilute sodium hydroxide solution yields 3-chloro-2-methylallyl alcohol.[9] The reaction may be represented by

$$CH_2ClC(CH_3)ClCH_2Cl + 2NaOH \longrightarrow CHCl{=}CCH_3CH_2OH + 2NaCl + H_2O$$

The rate of conversion is directly proportional to the alkalinity of the reagent and

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[4] W. J. Hale, U. S. P. 1,938,453, Dec. 5, 1933, to Dow Chemical Co., *Brit. Chem. Abs.*, **B**, 1934, 823; *Chem. Abs.*, 1934, **28**, 1047.

[5] A. L. Klebanskii and I. M. Dolgopol'skii, *J. Applied Chem. (U.S.S.R.)*, 1934, 7, 799, *Brit. Chem. Abs.* **A**, 1935, 193; *Chem. Abs.*, 1935, **29**, 2509. See Chapter 22.

[6] E. D. Hughes, *J.A.C.S.*, 1935, **57**, 708; *Brit. Chem. Abs.* **A**, 1935, 710; *Chem. Abs.*, 1935, **29**, 3298.

[6a] Velocity constant is the number of moles of reactant disappearing in one minute from a liter of solution containing a mole of reactant at all times.

[7] L. A. Clarke and L. W. Cook, U. S. P. 1,984,334, Dec. 11, 1934, to Texas Co.; *Brit. Chem. Abs.* **B**, 1935, 1085; *Chem. Abs.*, 1935, **29**, 812.

[7a] Pyrogallol is also employed in converting higher halides to alcohols.

[8] C. E. Sparks and R. E. Nelson, *J.A.C.S.*, 1936, **58**, 1010; *Brit. Chem. Abs.* **A**, 1936, 963; *Chem. Abs.*, 1936, **30**, 5177.

[9] A. O. Rogers and R. E. Nelson, *J.A.C.S.*, 1936, **58**, 1029; *Chem. Abs.*, 1936, **30**, 5176; *Brit. Chem. Abs.* **A**, 1936, 962.

TABLE 161.—*Yield of 1-Chloro-2-Methyl-2-Propanol.*

1,2-Dichloro-2-Methylpropane Moles	Water Liters	Reagent	Time of Refluxing Hours	1-Chloro-2-Methyl-2-Propanol Per Cent
1	4	Water	18.0	48
1	4	52 g. $CaCO_3$	4.5	46
0.5	4	26 g. $CaCO_3$	2.25	42
1	4	Water	18.0	41
1	4	52 g. $CaCO_3$	4.5	39
1	4	Water	17.5	38
1	4	52 g. $CaCO_3$	4.5	35
1	4	45 g. $Ca(OH)_2$	5.0	28
3	4	156 g. $CaCO_3$	12.0	28
1	4	95 g. $NaHCO_3$	5.0	20
1	4	52 g. $CaCO_3$	4.75	19
1	2	42 g. NaOH 2 l. water added slowly	4.25	7.9
1	4	95 g. NaOH	10.0	3.4

to the amount of water present. When two-thirds of the chlorine in the halide has been removed the reaction ceases. This may be seen from Fig. 179. 3-Chloro-2-methylallyl alcohol exists in *cis* and *trans* forms; the densities, indices of refraction and boiling points of the two are compared in Table 162.

TABLE 162.—*Cis- and Trans-3-Chloro-2-Methylallyl Alcohols*

Isomer	d_4^{25}	n_D^{20}	B.p., °C.
cis-3-Chloro-2-methylallyl alcohol........	1.1290	1.4737	160-162
trans-3-Chloro-2-methylallyl alcohol	1.1262	1.4730	166-168

The mixed chlorides of isobutene may be treated, under superatmospheric pressures, with aqueous solutions of alkalies at temperatures above 100°C., best at 220°C. The products are isobutene, isobutyl alcohol and *ter*-butyl alcohol, which can be separated by fractional distillation.[9a]

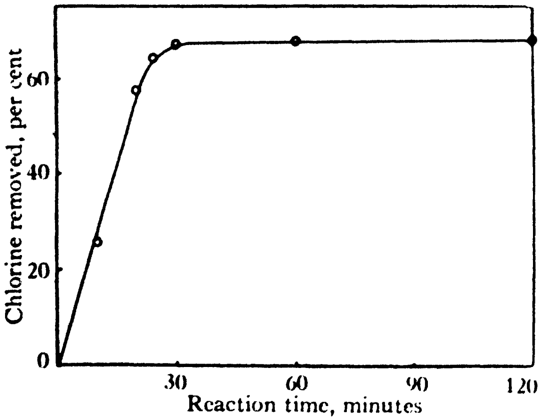

FIG. 179. Alkaline Hydrolysis of 1, 2, 3-Trichloro-2-Methylpropane. (A. O. Rogers and R. E. Nelson)

Courtesy Journal of American Chemical Society

Hughes[10] reports that the hydrolysis of *ter*-butyl chloride, like that of isopropyl chloride previously mentioned, is a unimolecular mechanism. The rate of reaction is dependent directly upon the velocity of ionization of the halide. When the latter is in excess, the speed of hydrolysis is constant and independent of the acidity or alkalinity of the medium. With a very dilute alcohol solution the velocity of reaction is also independent of the concentration of halide and water, but as the proportions of these latter increase, the rate of hydrolysis becomes more rapid. Woodburn and Whitmore[11] state that the speed of reaction is dependent upon the medium, being greater in pure water than in 5 per cent sodium carbonate solution. Some *ter*-butyl alcohol is formed when cold water is employed, but in hot water or in sodium carbonate solution olefins are obtained exclusively. A few results are listed in Table 163. Britton, Coleman and Warren[12] prepare *ter*-butyl alcohol by treating *ter*-butyl chloride with aqueous calcium hydroxide at 30-70°C. It is stated that any isobutyl chloride present will not undergo hydrolysis. To separate the alcohol from the unreacted chlorides, an azeotropic mixture of water, alcohol and chlorides is fractionally distilled. Fresh isobutyl chloride is added at intervals in quantities large enough to permit distillation of all the alcohol.[13]

[9a] E. G. Britton, G. H. Coleman and G. V. Moore, U. S. P. 2,067,473, Jan. 12, 1937, to Dow Chemical Co.; *Chem. Abs.*, 1937, **31**, 1432.

[10] E. D. Hughes, *J.C.S.*, 1935, 255; *Brit. Chem. Abs.* **A**, 1935, 452; *Chem. Abs.*, 1935, **29**, 2928.

TABLE 163. *Hydrolysis of ter-Butyl Chloride (25 cc.).*

Reagent	Cc.	Conditions	Time Min.	Halogen Reacted Per Cent
Water	50	Shake, cold	2	1.2
Water	50	Reflux	480	71.0
5% Na_2CO_3	50	Reflux	480	43.4

Butyl Bromide. Investigation of the action of dilute aqueous solutions of inorganic bases on isobutyl bromide[14] has shown that the extent of reaction increases with a rise in temperature, being 40 per cent complete after 10 hours at 85°C. as compared to 12-13 per cent at 60°C. It was also found that the rate of hydrolysis increases with dilution of the reagents. If the concentration of base becomes greater or if the temperature is raised, there is a tendency to olefin formation. The latter is also affected by the cation of the base, the lowest yield resulting with silver hydroxide, the highest with caustic potash. The results of this experiment are illustrated by Table 164.

TABLE 164. *Reaction of Isobutyl Bromide with Inorganic Bases.*

					Analysis of Products	
Base	Moles of Base	Soln. Cc.	Reaction Temp., °C.	% Reaction in 10 Hours	Olefins %	Alcohol %
KOH	0.89	200	85	40	64.1-65.5	34.5-35.9
KOH	.89	200	60	12-13	38.9-40.9	59.1-61.1
KOH	.44	500	85	58-61	47.8-49.7	50.3-52.2
KOH	.44	500	60		34.3	65.7
NaOH	1.25	200	60		25.6-27.8	72.2-74.4
AgOH	Excess	500	80		10.8-11	89 -89.2
HOH		500	80	0 (4 hours)		

The hydrolysis of *sec*-butyl bromide in 60 per cent ethyl alcohol has been studied by Hughes.[15] He reports that the reaction has a unimolecular mechanism in dilute alkaline and dilute acid solution. As the medium becomes more alkaline there is a greater amount of olefin formation, and hydrolysis becomes a bimolecular reaction. In slightly alkaline solution the velocity constant is 2.52, in acid, 2.44. According to French, McShan and Johler,[16] alcohols are the chief products of the hydrolysis of *sec*- and *ter*-butyl bromides, though some olefins are also obtained. The action of a number of bases on these bromides is summarized in Table 165.

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[11] H. M. Woodburn and F. C. Whitmore, *J.A.C.S.*, 1934, **56**, 1394; *Chem. Abs.*, 1934, **28**, 4375; *Brit. Chem. Abs.* **A**, 1934, 866.

[12] E. C. Britton, G. H. Coleman and G. W. Warren, U. S. P. 1,984,725, Dec. 18, 1934, to Dow Chemical Co.; *Brit. Chem. Abs.*, **B**, 1935, 1085; *Chem. Abs.*, 1935, **29**, 819.

[13] G. H. Coleman and G. W. Warren, U. S. P. 2,033,684, March 10, 1936, to Dow Chemical Co.; *Chem. Abs.*, 1936, **30**, 2986.

[14] H. E. French and W. H. Wade, *J.A.C.S.*, 1935, **57**, 1574; *Brit. Chem. Abs.* **A**, 1935, 1349; *Chem. Abs.*, 1935, **29**, 7270.

[15] E. D. Hughes, *J.A.C.S.*, 1935, **57**, 708; *Brit. Chem. Abs.* **A**, 1935, 710; *Chem. Abs.*, 1935, **29**, 3298

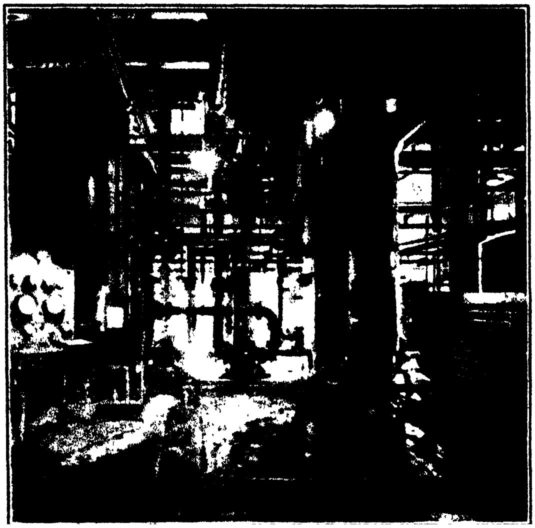

FIG. 180. View of Digester Unit for Hydrolysis of Amyl Chlorides. (L. H. Clark)

Courtesy Industrial and Engineering Chemistry

TABLE 165.—*Reaction of Butyl Bromides with Inorganic Bases.*

Bromide	Moles of Bromide	Base	Moles of Base	Reaction Temp. °C.	Time of Reaction Hrs.	Analysis of Products Olefins %	Alcohol %
sec-Butyl	0.061	AgOH	0.09	30-60	6	28.3-31.4	68.6-71.7
"	0.06	KOH	0.18	50	15	21.6	78.4
"	0.07	KOH	0.18	60	7.5	24	76
"	0.06	KOH	0.50	50	7.5	38.6	61.4
"	0.07	KOH	0.50	60	15	39.8	60.2
"	0.05	KOH	1.1	60	11	46.9	53.1
"	0.07	NaOH	0.50	60	7	34.7	65.3
"	0.08	NaOH	0.75	60	7	36.8	63.2
"	0.07	$Ca(OH)_2$	0.07	60	7.5	13.4	86.6
"	0.06	$Ca(OH)_2$	0.27	60	7	25.8	74.2
ter-Butyl	0.05	AgOH	0.08	30			99
"	0.12	AgOH	0.25	30			99
"	0.09	AgOH	0.15	40		0.2	99.6
"	0.05	AgOH	0.08	40		0.07	94.3
"	0.11	AgOH	0.20	60		2	96.2
"	0.05	AgOH	0.08	60		1	99
"	0.08	KOH	0.3	50		1.3	96.7
"	0.10	KOH	2.0	50			98.9
"	0.12	$Ba(OH)_2$	0.35	50		2.2	91.8
"	0.07	$Ba(OH)_2$	0.15	50		0.8	97.2

Amyl Chloride. The production of amyl alcohols and their acetates from chlorinated pentane has been conducted for a number of years.[17] A mixture of isomeric pentanes, obtained by fractional distillation of light petroleum, is chlorinated, heated under pressure with sodium oleate solution, and the amyl alcohols subsequently distilled off. This method yields all of the eight possible isomeric amyl alcohols. Campbell[18] reports the use of a semi-continuous process for the preparation of amyl alcohol from the corresponding chloride. The latter, with aqueous sodium hydroxide and amyl oleate (whose acid radical is a water-insoluble fatty acid) are placed in a reaction chamber and heated to 150°C. At intervals a portion of the liquid (containing oleic acid) is withdrawn from the bottom of the chamber, mixed with fresh chloride and alkali, heated and returned to the digester (see Fig. 181). In another method mono- and poly-chloropentanes may be treated with calcium hydroxide and sodium bicarbonate to furnish amyl alcohol.[19]

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[16] H. E. French, W. H. McShan and W. W. Johler, *J.A.C.S.*, 1934, **56**, 1346; *Brit. Chem. Abs.* **A**, 1934, 866; *Chem. Abs.*, 1934, **28**, 4372

[17] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. See also T. H. Durrans, *J.S.C.I.*, 1935, **54**, 585; *Brit. Chem. Abs.* **B**, 1935, 714; *Chem. Abs.*, 1935, **29**, 5541.

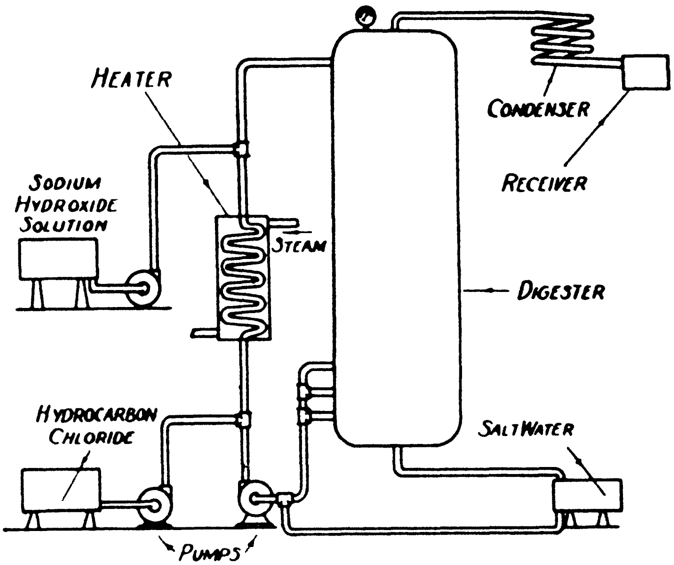

FIG. 181.—Semi-Continuous Method for Hydrolysis of Alkyl Halides. (C. L. Campbell)

When the temperature is maintained at 180-195°C., a 60 per cent conversion of halides in 40 to 60 minutes is reported. Clarke and Cook[20] suggest hydrolysis of the chloride with ferrous hydroxide at 75-150°C. to secure amyl alcohol. The optimum pressure is 300 pounds per square inch and the time of contact 4 hours. According to the above investigators a small amount of reducing agent (e.g., 1 per cent of pyrogallol) will inhibit aldehyde and acid formation. Ayres[21] recommends a method for separating products from reactants in the hydrolysis of chloropentanes. The products of the hydrolysis are said to be amylene (pentene), water, amyl chlorides (monochloropentane), higher boiling chlorides, and amyl alcohols. In the procedure these substances are placed in a flask heated by a steam coil.

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[18] C. L. Campbell, U. S. P. 1,953,745, April 3, 1934, to E. B. Badger & Sons Co.; *Brit. Chem. Abs.* **B**, 1935, 138; *Chem. Abs.*, 1934, **28**, 3740

[19] A. Dobryanskii, M. Davuidova and E. Margules, *J. Applied Chem.* (*U.S.S.R.*), 1933, **6**, 1122; *J. Inst. Pet. Tech.*, 1934, **20**, 608A; *Chem. Abs.*, 1934, **28**, 4035; *Brit. Chem. Abs.* **B**, 1934, 231.

[20] L. A. Clarke and L. W. Cook, U. S. P. 1,984,334, Dec. 11, 1934, to Texas Co.; *Brit. Chem. Abs.* **B**, 1935, 1085; *Chem. Abs.*, 1935, **29**, 812.

[21] E. A. Ayres, Jr., U. S. P. 1,926,189, Sept. 12, 1933, to Fidelity Philadelphia Trust Co.; *Brit. Chem. Abs.* **B**, 1934, 534; *Chem. Abs.*, 1933, **27**, 5751.

The flask is connected through a rectifying column to a condenser which is, in turn, connected to a decanter and receivers (see Fig. 182). In the distillation the first compound which comes over is amylene, which may be seen from Fig. 183. An intermediate fraction containing amylene and amyl chloride is then taken off under reflux. As the temperature rises to 76°C. a constant boiling mixture of amyl chloride and water is removed. This mixture is conducted to the decanter where the water is separated and the halide returned to the distillation flask. If this step is effected without employing a reflux condenser, the removal of water is said to be facilitated, since a constant boiling mixture of amyl alcohol and water also comes over at this temperature. In this case, the chloride and alcohol are returned to the flask. Amyl chloride is next removed from the distilling flask by heating under a reflux condenser. The fraction which is secured is reported to contain some

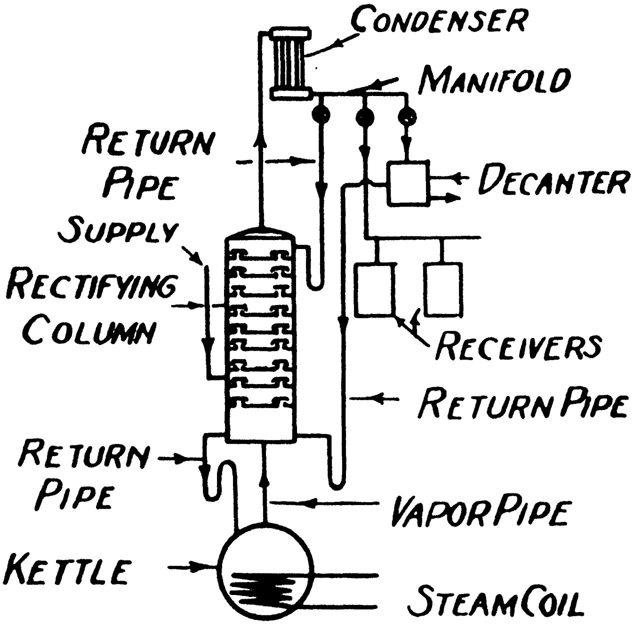

Fig. 182.—Diagram of Method for Separating Reactants from Products of Chloropentane Hydrolysis. (E. E. Ayres, Jr.)

Table 166.—*Reaction of ter-Amyl Chloride (0.061 Mole) with Inorganic Bases.*

Base	Moles of Base, 300 Cc. of Solution	Reaction Temp., °C.	Time of Reaction Hours	Extent of Reaction, %	Analysis of Products(%)	
					Olefin	Alcohol
AgOH	0.0805	45	10	82-87	13.7-14.5	85.5-86.3
AgOH	.0805	35	12	89-91	8.4-8.8	91.2-91.6
$Ba(OH)_2$	.061	45	10	76-80	16.0-16.8	83.2-84
$Ba(OH)_2$	.076	45	10	85-86	25.6-25.8	74.2-74.4
$Ba(OH)_2$	.076	35	12	76-82	14.0-15.0	85.0-86.0
$Ca(OH)_2$	.094	45	10	86-88	16.4-17.8	82.2-83.6
LiOH	.123	45	10	77	16.6-17.8	82.2-83.4
NaOH	.132	45	10	86-88	17.8-18.3	81.7-82.2
KOH	.123	45	10	80-81	19.3-20.8	79.2-80.7
KOH	.123	35	12	65	12.5-13.4	86.6-87.5

amyl alcohol. At this point all the water and amyl chlorides are stated to be removed from the flask, but there still remains, in addition to amyl alcohol, some higher boiling chlorides. The latter are separated by adding 5 per cent of water to the residue in the still. In this manner a constant boiling mixture of the higher chlorides and water is taken off, leaving amyl alcohol as the residue.

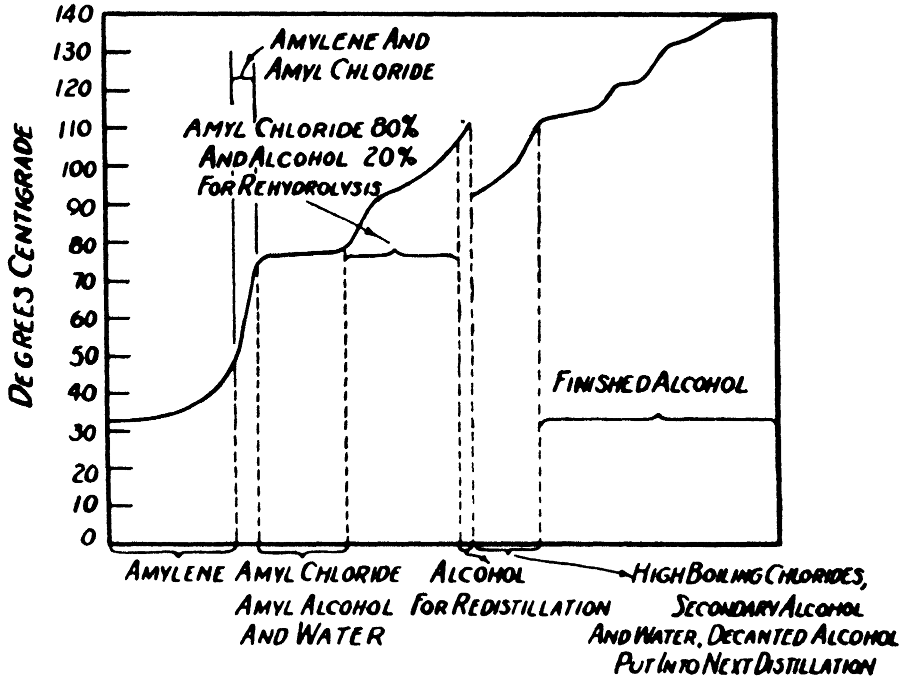

FIG. 183.—Typical Distillation Curve for Method of Fig. 182.

The action of various inorganic bases on *ter*-amyl chloride and bromide gives *ter*-amyl alcohol as the main product, together with some olefins.[22] The yield of the latter becomes greater with increasing temperatures and higher concentrations of hydroxide. The investigators also state that lithium, sodium and potassium hydroxide, in the order written, favor olefin production. Note Tables 166 and 167.

TABLE 167. *Reaction of ter-Amyl Bromide (0.057 Mole) with Inorganic Bases. Extent of Reaction = 100 Per Cent.*

Base	Moles of Base, 300 Cc. of Solution	Reaction Temp., °C.	Time of Reaction Hours	Analysis of Products (%) Olefin	Analysis of Products (%) Alcohol
AgOH	0.074	45	10	8.7-10.4	89.6-91.3
AgOH	.074	35	12	4.6-5.2	94.8-95.4
$Ca(OH)_2$	.069	45	10	11.3-12.0	88.0-88.7
NaOH	.13	45	10	12.9-13.5	86.5-87.1
KOH	.123	45	10	14.0-15.4	84.6-86.0
KOH	.123	35	12	11.2-11.5	88.5-88.8
$Ba(OH)_2$	.073	45	10	18.7-19.8	80.2-81.3
$Ba(OH)_2$	.073	35	12	11.5-11.6	88.4-88.5

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[22] H. E. French and A. E. Schaefer, *J.A.C.S.*, 1935, 57, 1576; *Brit. Chem. Abs.* A, 1935, 1349, *Chem. Abs.*, 1935, 29, 7271.

Chapter 34

Miscellaneous Reactions of Halogen Derivatives of Paraffins and Cycloparaffins

The chloro derivatives of the paraffin series are in general less reactive than the alkyl bromides and iodides, but this holds true only if the structure of the paraffin molecule is alike in the three halides. The primary substituted derivatives are less reactive than the secondary, but the tertiary undergo some reactions with remarkable ease. The latter halides, however, do not react with salts of organic acids or with alcoholic ammonia to form esters and amines, respectively, but instead are transformed, in part, to the corresponding olefin.

Because of the large number of alkyl halides[1] and the wide scope of their chemical reactivity, the following comments have been limited to include only some of the more interesting and important applications. Among these are:

(1) Production of olefins and hydrogen halides.[2]

$$C_nH_{(2n+1)}X \longrightarrow C_nH_{2n} + HX$$

(2) Condensation with alcoholic ammonia or with amines to yield alkylamines.

$$C_nH_{(2n+1)}X + NH_3 \longrightarrow C_nH_{(2n+1)}NH_2 + HX$$

(3) Condensation with hydrocarbons, or derivatives of hydrocarbons, under the influence of Friedel-Crafts condensing agents.

$$C_2H_{(2n+1)}X + C_6H_6 \xrightarrow{AlCl_3} C_nH_{(2n+1)}C_6H_5 + HX$$

(4) Reaction with sodium, potassium or ammonium sulphite to form sulphonates by what is called the Strecker reaction.

$$C_nH_{(2n+1)}X + Na_2SO_3 \longrightarrow C_nH_{(2n+1)}SO_3Na + NaX$$

(5) Replacement of halogen by acid radicals such as $-CN$ and $-SH$ through interaction with salts of these acids.

$$C_nH_{(2+1)}X + KCN \longrightarrow C_nH_{(2n+1)}CN + KX$$

(6) Interaction with metallic magnesium to yield Grignard compounds applicable in numerous syntheses.

$$C_nH_{(2n+1)}X + Mg \longrightarrow C_nH_{(2n+1)}MgX$$

(7) Reaction with alkali alcoholates or phenates to yield ethers.

$$C_nH_{(2n+1)}X + NaOR \longrightarrow C_nH_{(2n+1)}OR + NaX$$

Bell and Clark[3] have made a comparison of the preparation of unsaturated hydrocarbons from a number of halides by reaction with potassium hydroxide and with quinoline. The hydroxide, when united with *n*-halides, gave poor yields of olefins, possibly because of ether formation. On the other hand, good results were obtained with secondary, tertiary and cyclic halides. Quinoline was recommended for the preparation of unsaturated hydrocarbons from all normal halides and from secondary halides of low molecular weight. Under the same conditions of temperature and pressure, bromides and iodides furnish a greater proportion of olefins than do chlorides.

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[1] For the number of mono- and di-substituted products, see Chapter 30.

[2] X represents an atom of chlorine or other halogen.

[3] A. Bell and R. H. Clark, *Trans. Roy. Soc. Can.*, 1935, **29** (3), 61; *Brit. Chem. Abs.* **A**, **1936**, 451; *Chem. Abs.*, 1936, **30**, 2547.

DECOMPOSITION OF ALKYL HALIDES INTO OLEFINS

The alkyl halides may be decomposed to yield olefins and hydrogen halides by the action of alkalies or alkali salts of organic acids as well as by heat with or without catalysts.[4] When alkalies are employed in aqueous or alcoholic solution, ethers and alcohols are produced in addition to the unsaturated hydrocarbons. Under the influence of heat, dechlorination is a reversible process in which the point of equilibrium of the equation $C_nH_{(2n+1)}X \rightleftarrows C_nH_{2n} + HX$ is displaced to the right with rising temperatures. Temperatures of 450-500°C. are required in order to remove chlorine from methyl chloride, but for the iodide the range may be restricted to 270-320°C.

When ethyl chloride is heated to 510-600°C. in the presence of pumice, ethylene is secured, the products of the reaction containing from 55 to 76 per cent of the unsaturated hydrocarbon. Yamaguchi[5] has made a study of some of the factors influencing the thermal dechlorination of tetrachlorethane. The use of activated carbon and of temperatures of 250-300°C. lead only to trichloroethylene. A temperature of 400°C. was necessary to produce ethylene. A small amount of ammonium hydroxide serves to accelerate the dechlorination, but ethyl alcohol has an inhibitory effect, as do the chlorides of nickel and barium. Aralkyl chlorides may also be employed as reactants to furnish unsaturated compounds. For example α-chloroethylbenzene may be treated with benzoic acid to obtain phenylethylene (styrene) and hydrochloric acid.[6] Evolution of hydrogen chloride begins at 130-140°C., the optimum temperature range being 150-200°C. The styrene is distilled from the reaction zone as quickly as it is formed, thus separating it from any unreacted chloroethylbenzene. The distillate is washed with sodium carbonate and fractionated, the portion boiling at 146°C. being retained. The unsaturated compound tends to polymerize[7] but this change can be prevented by having present a small proportion of nitrobenzene. According to Olivier and Weber[8] the bromides of ethane, on hydrolysis, will furnish ethylene. In one case 300 cc. of either 1,2-dibromoethane or ethylidene bromide were dissolved in 900 cc. of water and 300 cc. of acetic anhydride. A small amount (1 per cent) of 0.375 molar sulphuric acid was added and the temperature maintained at 60°C.

Senderens[9] points out that propyl chloride will not undergo dechlorination by heating to 140-280°C. unless a contact agent is present. Among those recommended are aluminum oxide at 280°C., thorium oxide at 260°C., zirconium oxide at 250°C., hydrous aluminum silicate (kaolin) at 230°C., calcium phosphate at

[4] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[5] S. Yamaguchi, *J. Chem. Soc. Japan*, 1934, 55, 1227; *Brit. Chem. Abs.* **A**, 1936, 311; *Chem. Abs.*, 1935, **29**, 4326.

[6] W. Krey, U. S. P. 2,005,042, June 18, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 5127.

[7] For a discussion of the polymerization of styrene see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[8] S. C. J. Olivier and A. Ph. Weber, *Rec. trav. chim.*, 1934, 53, 1087; *Chem. Abs.*, 1935, **29**, 1383; *Brit. Chem. Abs.* **A**, 1935, 62. See also S. C. J. Olivier, *Rec. trav. chim.*, 1936, 55, 567; *Brit. Chem. Abs.* **A**, 1936, 1090; *Chem. Abs.*, 1936, **30**, 7017.

[9] J. B. Senderens, *Compt. rend.*, 1935, **200**, 612; *Brit. Chem. Abs.* **A**, 1935, 1064; *Chem. Abs.*, 1935, **29**, 2874.

260°C., anhydrous barium chloride at 270°C., and anhydrous calcium chloride at 265°C. These catalysts have also been found to aid the transformation of 1-chlorobutane to 1-butene and hydrogen chloride. However, in the case of 2-chlorobutane the dimethylethylene which results will recombine with the hydrogen chloride unless the two are separated rapidly, which may be accomplished by fractionation. Calcium oxide may also be used as a promoter in the dechlorination of butyl chloride.[10] Formation of butene begins at 275°C. but the optimum temperature is 285°C. The contact agent reacts with the resulting hydrogen chloride to form calcium chloride. The latter is said to catalyze the reaction so that the temperature may then be reduced to 225°C. without affecting the yield of olefins. Dechlorination of *ter*-butyl chloride has been accomplished without the aid of promoters.[11] The reaction was conducted in a flask coated on the inside with carbon, and the temperature was varied for different runs between 547-645°K. (820-918°C.). The reaction is reported to be homogeneous and unimolecular with an energy of activation of 45,000 ± 1900 cal.

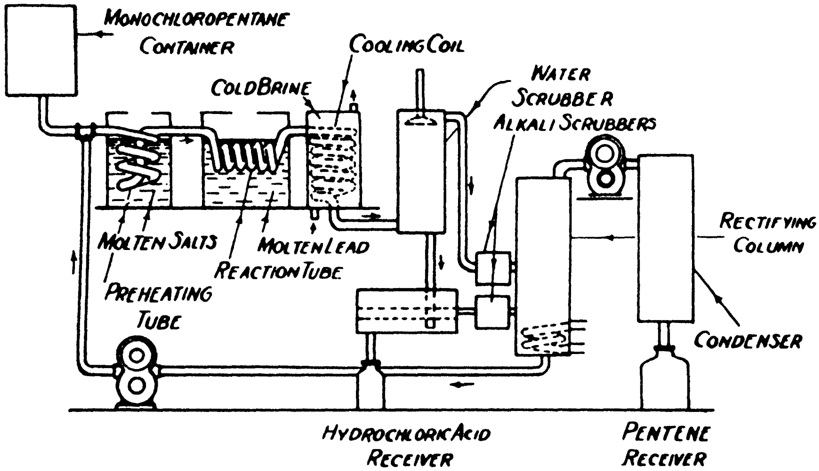

FIG. 184.—Sketch of Equipment for Production of Olefins from Alkyl Halides. (H. B. Hass and P. E. Weston)

Although the bromides of butane furnish olefins more readily than do the chlorides, there is an almost immediate recombination of the reaction products so that separation of the latter is rather difficult. This has been noted by Senderens[12] when forming dimethylethylene and hydrogen bromide by heating isobutyl bromide with thorium oxide at 200°C. and butyl bromide with the oxides of aluminum and thorium at 280-300°C.

Hass and Weston[13] point out that the dehalogenation of a mixture of 2-bromo and 3-bromopentane may be utilized to prepare 1-pentene and 2-pentene. The halides are led through a preheating tube where they are vaporized (see Fig. 184). The vapors are then conducted into a reaction chamber, heated to 500°C. by a bath of molten lead. After a contact period of 1.5-2 seconds, the reaction products are cooled to 20°C., washed with water, and fractionated to separate the pentenes from hydrobromic acid and unreacted halides. The latter may then be recycled. Thermal decomposition of *ter*-amyl chloride at 543-600°K. (816-873°C.) is said to follow a unimolecular, homogeneous reaction having an activation energy of 46,200 ± 700 cal.[14]

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[10] J. B. Senderens and J. Aboulenc, *Compt. rend.*, 1936, **202**, 104; *Chem. Abs.*, 1936, **30**, 2547; *Brit. Chem. Abs.* **A**, 1936, 452.

[11] D. Brearley, G. B. Kistiakowsky and C. H. Stauffer, *J.A.C.S.*, 1936, **58**, 43; *Chem. Abs.*, 1936, **30**, 2088; *Brit. Chem. Abs.* **A**, 1936, 295.

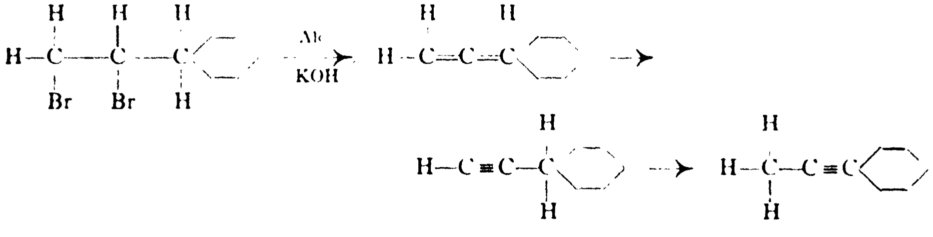
[12] J. B. Senderens, *Compt. rend.*, 1935, **200**, 2137; *Chem. Abs.*, 1935, **29**, 6496; *Brit. Chem. Abs.* **A**, 1935, 1103.

[13] H. B. Hass and P. E. Weston, U. S. P. 1,975,456, Oct. 2, 1934, to Purdue Research Foundation; *Brit. Chem. Abs.* **B**, 1935, 839; *Chem. Abs.*, 1934, **28**, 7260.

Monochlorinated paraffins containing more than 8 carbon atoms are reported to give olefins and diolefins on dehalogenation. Ward and Fulweiler[15] point out that at 180°C. potassium cresolate reacts with chloro-2,7-dimethyloctane to furnish decene. A yield of 91.6 per cent of an olefin boiling between 159.6 and 162.8°C. was obtained which would correspond to 2,7-dimethyloctene (boiling between 159-162°C.) secured by Kishner.[16] Also, it has been suggested that dehalogenation of a chlorinated kerosene fraction (b.p. 243-258°C.) may be effected to yield unsaturated aliphatic hydrocarbons.[16a] Thermal treatment of polychlorinated paraffin hydrocarbons is said to form products applicable as lubricants.[17] For example, a paraffin containing 42 per cent of chlorine was heated to 300°C. yielding a product having a high viscosity and flash point and a low melting point (−20°C.).

Substances capable of reacting with hydrogen chloride may be employed in dehalogenation. For example, reaction of 1,2,3,4-tetrachlorobutane with potassium hydroxide in methyl alcohol at 10° to 18°C. is said to yield butadiene.[18]

Aralkyl dihalides have also been dehalogenated. According to Zeberg[19] solid potassium hydroxide caused dehalogenation of 1,2-dibromo-3-phenylpropane at a temperature of 110°C. with alcohol as a solvent. Phenylallene was first formed and then underwent isomerization first to benzylacetylene and later to methylphenylacetylene.



An interesting sidelight on dehalogenation has been noted by Sandonnini and Borghello.[20] Electrolysis of carbon tetrachloride in a 10 per cent sulphuric acid solution, employing a platinum anode and a lead cathode, gave chloroform (trichloromethane) and dichloromethane rather than olefins.

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[14] D. Brearley, G. B. Kistiakowsky and C. H. Stauffer, *loc. cit.*

[15] A. L. Ward and W. H. Fulweiler, *J.A.C.S.*, 1934, **56**, 1641; *Chem. Abs.*, 1934, **28**, 5037; *Brit Chem. Abs.* **A**, 1934, 989.

[16] N. Kishner, *J. Russ. Phys.-Chem. Soc.*, 1900, **32**, 381; *Chem. Zentr.*, 1900, **2**, 725.

[16a] C. A. Thomas and J. F. Olin, U. S. P. 2,065,323, Dec. 22, 1936, to Sharples Solvent Corp.; *Chem. Abs.*, 1937, **31**, 1192.

[17] Y. Tanaka, R. Kobayashi and H. Furumoto, *J. Soc. Chem. Ind., Japan*, 1933, **36**, 228B; *Brit. Chem. Abs.* **B**, 1933, 738; *Chem. Abs.*, 1933, **27**, 3443.

[18] W. H. Carothers and G. J. Berchet, U. S. P. 1,998,442, April 23, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 3692; *Brit. Chem. Abs.* **B**, 1936, 487. *Cf.* I. E. Muskat, U. S. P. 2,070,609, Feb. 16, 1937, to E. I. du Pont de Nemours & Co. For rates of decomposition of olefin dihalides, see W. Taylor, *J.C.S.*, **1935**, 1514; *Chem. Abs.*, 1936, **30**, 2085; *Brit. Chem. Abs.* **A**, 1935, 1465. and R. A. Ogg, Jr., *J.A.C.S.*, 1936, **58**, 607; *Chem. Abs.*, 1936, **30**, 4077; *Brit. Chem. Abs.* **A**, 1936, 684.

[19] E. F. Zeberg, *J. Gen. Chem. (U.S.S.R.)*, 1935, **5**, 1016; *Brit. Chem. Abs.* **A**, 1936, 51; *Chem. Abs.*, 1936, **30**, 1023.

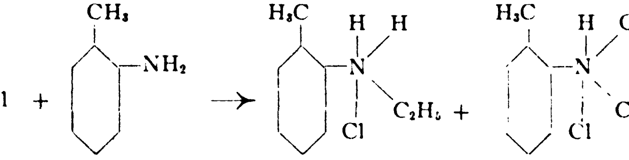
[20] C. Sandonnini and V. N. Borghello, *Atti accad. Lincei*, 1934, **20**, 334; *Brit. Chem. Abs.* **A**, 1935, **604**; *Chem. Abs.*, 1935, **29**, 3920.

REACTION OF CHLORINATED PARAFFINS AND CYCLOPARAFFINS WITH AMMONIA AND AMINES

The primary and secondary alkyl halides react with ammonia and amines to form alkylamines, whereas the tertiary halides yield only olefins on similar treatment. The condensation usually takes place in alcoholic solutions with moderate heating (100°C.) and primary, secondary and tertiary amines result as well as quaternary compounds in some cases.[21] The ammonolysis of ethyl chloride may be represented by

$$\begin{array}{l} C_2H_5Cl + NH_3 \rightarrow C_2H_5NH_2 + HCl \\ C_2H_5Cl + C_2H_5NH_2 \rightarrow (C_2H_5)_2NH + HCl \\ C_2H_5Cl + (C_2H_5)_2NH \rightarrow (C_2H_5)_3N + HCl \\ C_2H_5Cl + (C_2H_5)_3N \rightarrow (C_2H_5)_4NCl \end{array}$$

Tolmachev[22] reports that the reaction of ethyl chloride with an aromatic compound such as *o*-toluidine leads to ethyl *o*-tolyl and diethyl *o*-tolyl ammonium chloride according to the equation:



If an autoclave is employed in which temperatures of 170-200°C. are maintained, the yields are independent of an excess of halide or of the length of heating time. With molar quantities of reactants 70 mole per cent of the ethyl and 15 mole per cent of the diethyl compound are formed. According to Carleton and Woodward,[23] ethyl chloride will form a secondary and tertiary amine with aniline if the two are reacted in ethanol solution. Thus, 465 g. of aniline, 208 g. of ethyl chloride and 250 g. of ethanol were heated for 5 hours at 180-185°C. under a pressure of 175-225 lbs. per square inch. At the end of the contact period, the mixture was made alkaline and the oil layer separated. The latter was stated to consist of 60 per cent of monoethylaniline and 40 per cent of diethylaniline. The chloride will also undergo condensation with α-naphthylamine if solvents are excluded from the reaction zone.[24] The temperature should not exceed 155°C. during the reaction, and in the final stages should be lowered to 140°C. The products of the ammonolysis include ethyl-α-naphthylamine.

To prepare ethylenediamine, Curme and Lommen[25] suggest treatment of dichloroethane with excess aqueous ammonia at a temperature of 110°C. and a pressure of 10 atmospheres. The reactants are conducted into a pressure-tight reaction vessel where they are admixed under the conditions mentioned above. A portion of the reaction products, reported to consist of an aqueous solution of ethylenediamine hydrochloride, ammonium chloride and ammonia, is withdrawn intermittently from the reaction zone (see Fig. 185). The mixture is then conducted to a fractionating column where it is heated with aqueous caustic soda. In this manner ethylenediamine is said to be formed and ammonia released from the ammonium halide. The ammonia is returned to the reaction vessel and the diamine drawn off.

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[21] Carleton Ellis "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[22] N. A. Tolmachev, *Trans. Leningrad Chem.-Tech. Inst.*, 1934, 1, 119; *Chem. Abs.*, 1935, 29, 2930.

[23] P. W. Carleton and J. O. Woodward, U. S. P. 1,994,851, March 19, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1936, 265; *Chem. Abs.*, 1935, 29, 2973.

[24] P. W. Carleton and E. L. Mattison, U. S. P. 2,039,390, May 5, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, 30, 4176.

[25] G. O. Curme and F. W. Lommen, U. S. P. 1,832,534, Nov. 17, 1931, to Carbide and Carbon Chem. Corp.; *Brit. Chem. Abs.* B, 1932, 973; *Chem. Abs.*, 1932, 26, 999.

Some of the physical constants[26] of the diamine are listed in Table 168.

TABLE 168.—*Physical Constants of Ethylene Diamine.*

Specific gravity 20°/20°C.	0.8994
Grams/liter at 20°C.	899
Molecular weight	60.08
Boiling point, °C.	116.2
Vapor pressure at 20°C., mm.	10.0
Melting point, °C.	11.0
Flash point, °C.	33.9
Refractive index at 26°C.	1.4540
*p*H of 25% soln. at 25°C.	11.9
Latent heat of vaporization, cal./gram	167
Latent heat of fusion at 0°C., cal./gram	77
Heat of solution at 15°C., Cal./mole	7.6
Heat of combustion, Cal./mole	452.6

Ethlylenediamine is reported to be effective as a solvent for certain vat dyes, as a stabilizer for latex and as a corrosion inhibitor.[27] It has also been recommended for maintaining the color of mineral lubricating oils during refining of the latter.[27a] For this purpose 0.1-0.005 per cent of the diamine is said to be sufficient. The higher fatty acid soaps such as oleyl ethylene diamine are suggested as detergents for use in acid solutions.[28] Caspe[29] proposes to use diethylamine as a reactant in the manufacture of tertiary amines. In this procedure 1 mole of isopropyl bromide, 1 mole of diethylamine and 0.5 mole of glycerol are heated

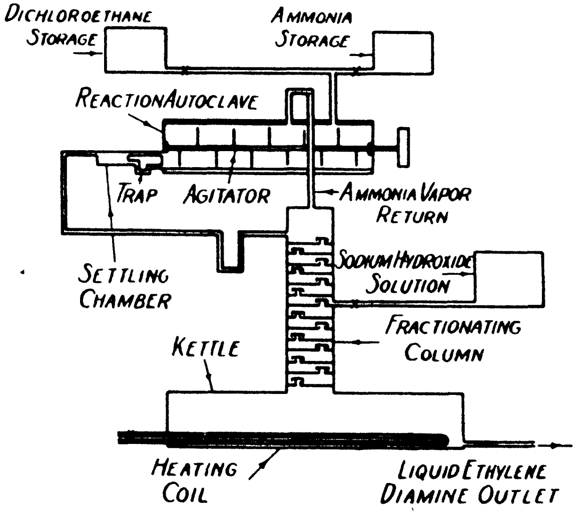

FIG. 185. Formation of Ethylene Diamine from Dichloroethane. (G. O. Curme, Jr., and F. W. Lommen)

under a reflux condenser for several days. The composite is then made alkaline with sodium hydroxide, extracted with ether, and distilled to secure the fraction boiling between 108 and 109°C. which contains diethylisopropylamine.

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[26] A. L. Wilson, *Ind. Eng. Chem.*, 1935, **27**, 867; *Brit. Chem. Abs.* **B**, 1935, 893; *Chem. Abs.*, 1935, **29**, 6571.

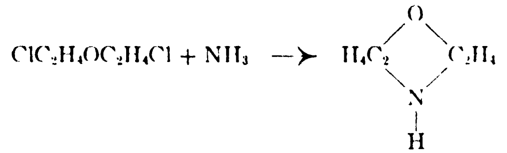
[27] A. L. Wilson, *loc. cit.*

[27a] V. Voorhees, U. S. P. 1,973,676, Sept. 11, 1934, to Standard Oil Co. of Ind.; *Brit. Chem. Abs.* **B**, 1934, 759; *Chem. Abs.*, 1934, **28**, 6999.

[28] M. Hartmann and H. Kägi, U. S. P. 1,527,868, Feb. 24, 1925; *Chem. Abs.*, 1925, **19**, 1757; *J.S.C.I.*, 1925, **44**, 300B.

[29] S. Caspe, U. S. P. 1,993,542, March 5, 1935; *Brit. Chem. Abs.* **B**, 1936, 442; *Chem. Abs.*, 1935, **29**, 2547.

One method for the preparation of morpholine is by reaction of *sym*-dichlorodiethyl ether and ammonia.[30] The reaction zone consists of an autoclave in which a temperature of 50°C. and a pressure of 1750 pounds per square inch are maintained. The condensation may be represented by the equation,



The product is said to be efficacious as a solvent for dyes, a corrosion inhibitor for water solutions, a color stabilizer for petroleum products, an antiknock agent for gasoline, and a carbon remover for aluminum pistons.[31]

Olin[32] reports that the product obtained by chlorinating a mixture of pentanes will yield mono- and diamylamines if reacted with an excess of ammonia. The amyl chlorides (1065 g.) and ammonia (680 g.) are dissolved in anhydrous ethanol. The temperature is maintained at 100-110°C. for 5 hours. Then the mixture is cooled to 20°C. and the solvent and excess ammonia distilled, leaving a residue of amyl ammonium chloride. Steam is introduced and caustic soda added to separate the amines from hydrogen chloride and unreacted amyl chloride. Two layers form, the upper containing the amines which may be fractionated to separate the mono- and diamylamines, the former boiling between 85 and 110°C., the latter above 110°C.

The halides of the higher members of the paraffin series may also be used to form primary and secondary amines. In one process octadecyl chloride is incorporated with 60-65 per cent ammonium hydroxide and the mixture heated in a closed vessel for 5 hours at 120-170°C.[33] According to Pyman and Levene[34] a secondary amine is obtained by heating 1,10-dichlorodecane with diamylamine, $(C_2H_5)_2NH$. The product, 1,10-bis(diamylino)decane, is said to be efficient in destroying microscopic organisms such as the amoeba. Also, it has been proposed[35] that a dichlorinated paraffin oil boiling about 150°C. be condensed with ammonia (in ethyl alcohol) at 160-170°C. The viscous oil which results is suggested as an acid soap in dyeing.

Wright and Bergstrom[36] point out that potassium amide reacts with an excess of phenyl chloride, bromide or iodide to give aniline, diphenylamine and a small proportion of triphenylamine. The condensation takes place in a liquid ammonia solution at −33°C.

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[30] A. W. Campbell, U. S. P. 2,034,427, March 14, 1936, to B. F. Goodrich Co.; *Chem Abs.*, 1936, **30**, 2986.

[31] A. L. Wilson, *Ind. Eng. Chem.*, 1935, **27**, 867; *Chem. Abs.*, 1935, **29**, 6571; *Brit. Chem. Abs* **B**, 1935, 893.

[32] J. F. Olin, U. S. P. 2,006,058, June 25, 1935, to Sharples Solvents Corp.; *Chem. Abs.*, 1935, **29**, 5458.

[33] British P. 437,530, 1935, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1936, 89; *Chem. Abs.*, 1936, **30**, 2201. French P. 784,559, 1935; *Chem. Abs.*, 1936, **30**, 107.

[34] F. L. Pyman and H. H. L. Levene, U. S. P. 2,056,867, Oct. 6, 1936, to Boot's Pure Drug Co. Ltd.; *Chem. Abs.*, 1936, **30**, 8241. British P. 433,086, 1935; *Chem. Abs.*, 1936, **30**, 574; *Brit. Chem. Abs.* **B**, 1935, 973.

[35] K. Keller, U. S. P. 1,948,924, Feb. 27, 1934, to General Aniline Works; *Chem. Abs.*, 1934, **28**, 2723.

[36] R. E. Wright and F. W. Bergstrom, Paper given at Amer. Chem. Soc. Meeting, San Francisco, 1935.

CONDENSATION AND ALKYLATION BY MEANS OF ALKYL HALIDES

Under certain conditions the alkyl halides may be polymerized or may be employed to form condensation products or to introduce alkyl groups into aromatic compounds. In the latter case, benzene, toluene, naphthalene and the phenols comprise the general aromatic groups. The condensing agent usually employed is anhydrous aluminum chloride, though certain other chlorides are also effective. Some of the generalities regarding the Friedel-Crafts syntheses, as these reactions are called,[37] are summarized by Calloway[38] as follows:

1. Alkylation by means of this synthesis is a reversible reaction applicable to practically all types of organic compounds.
2. Acylations are essentially nonreversible and may be applied to a variety of reactants.
3. Rearrangements are prevalent in alkylation but acylation proceeds without rearrangement.
4. The orientation of entering groups is essentially that found in other substitution reactions.
5. A variety of condensing agents may be used, but aluminum chloride is apparently the most active.
6. The Friedel-Crafts reaction is catalytic, and there is apparently no formation of intermediate organoaluminum substances.

Prins and Englehard[39] reported that trichloromethane (chloroform) reacted with dichloroethylene ($C_2H_2Cl_2$) in the presence of anhydrous aluminum chloride to form 1,1,2,3,3-pentachloropropane according to the equation:

$$C_2H_2Cl_2 + CHCl_3 \xrightarrow{AlCl_3} CHCl_2CHClCHCl_2$$

The chloroform and olefin halide were separately heated for a few minutes with 1 per cent of the condensing agent and cooled. A mixture of 120 g. of the chloroform and 97 g. of dichloroethylene was then saturated with the aluminum halide and heated to 50°C. for 2 hours, giving a yield of 70 per cent of the pentahalide. It was pointed out that a number of high-boiling condensation products also result. The latter react with the dissolved aluminum chloride, rendering the catalyst inactive. Treatment of dichlorofluoromethane with a Friedel-Crafts condensing agent at 8 to 25°C. and at atmospheric pressure leads to difluorochloromethane and chloroform.[40] At 45°C. and at the same pressure, trichlorofluoromethane furnishes dichlorodifluoromethane and tetrachloromethane. In both cases a fluorine atom on one molecule is substituted for a chlorine atom on another molecule.

It has been proposed that dichloroethane be condensed with vinyl chloride in the presence of aluminum chloride.[40a] When the temperature is maintained below 60°C. the product is stated to be trichlorobutane. Under similar conditions, dichloroethane combines with *sym*-dichloroethylene to yield tetrachlorobutane, and with trichloroethylene to furnish pentachlorobutane.

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[37] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[38] N. O. Calloway, *Chem. Revs.*, 1935, 17, 327; *Chem. Abs.*, 1936, **30**, 2181.

[39] H. J. Prins and J. W. Englehard, *Rec. trav. chim.*, 1935, **54**, 307; *Chem. Abs.*, 1935, **29**, 3977; *Brit. Chem. Abs.* **A**, 1935, 605.

[40] C. W. Croco, U. S. P. 1,994,035, March 12, 1935, to Kinetic Chemicals, Inc.; *Brit. Chem. Abs.* **B**, 1936, 441; *Chem. Abs.*, 1935, **29**, 2974.

[40a] British P. 453,414, 1936, to Consortium für elektrochemische Industrie G.m.b.H ; *Brit. Chem. Abs.* **B**, 1936, 1140; *Chem. Abs.*, 1937, **31**, 1046.

Prins[41] noted that aluminum chloride can also be utilized to prepare hexachloropropene from pentachloroethane. With 1.5 per cent of condensing agent a temperature of 100-110°C. was maintained for 1.5 hours to give a 95 per cent yield of tetrachloroethylene. The latter was boiled for 10 minutes with 1.5 molecular equivalents of trichloromethane to form heptachloropropane in 85 per cent yield. This product was heated with tetrachloromethane and aluminum chloride at 60-70°C. to secure hexachloropropene. The three steps of the synthesis are summarized by the equations,

$$\begin{aligned} C_2HCl_5 &\longrightarrow C_2Cl_4 + HCl \\ C_2Cl_4 + CHCl_3 &\longrightarrow CHCl(CCl_3)_2 \\ CHCl(CCl_3)_2 + CCl_4 &\longrightarrow CCl_3CCl{=}CCl_2 \end{aligned}$$

A process in which a lubricating oil is treated with amyl chloride and a small amount of the chloride of aluminum has been proposed.[42] A contact time of 2 hours at 80°C. is said to increase the refractive index and reduce the amount of carbon residue in the oil. For example, 100 volumes of lubricating oil were admixed with 10 per cent of aluminum chloride and with 30 volumes of amyl chloride. The temperature was maintained at 175°F. (79°C.) for 2 hours. At the end of that time the mixture was conducted to a sludge separator where the aluminum chloride was removed (see Fig. 186). The oil may then be "sweetened" with sulphuric acid and clay or by steam to produce the finished oil. A composition said to be efficient as a dielectric may be obtained by polymerization of halogenated paraffins.[43] In one instance 1,2,2-trichloroethane is heated to 85°C. with 0.1-0.5

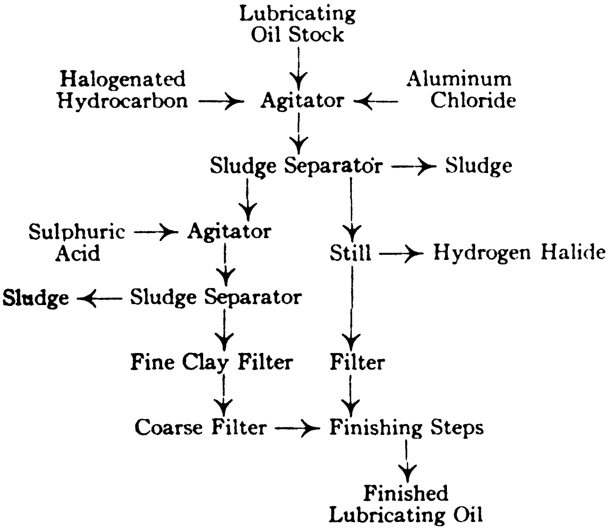

FIG. 186.
Flow Sheet for Treatment of Lubricating Oils with Amyl Chloride and Aluminum Chloride. (E. Ayres and H. G. Smith)

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[41] H. J. Prins, *Rec. trav. chim.*, 1935, 54, 249; *Chem. Abs.*, 1935, 29, 3298; *Brit. Chem. Abs.* A, 1935, 470.

[42] E. Ayres and H. G. Smith, U. S. P. 2,010,387, Aug. 6, 1935, to Gulf Refining Co.; *Brit. Chem. Abs.* B, 1936, 731; *Chem. Abs.*, 1935, 29, 6418.

[43] British P. 430,298, 1935, to British Thomson-Houston Co. Ltd.; *J. Inst. Pet. Tech.*, 1935, 21, 344A; *Chem. Abs.*, 1935, 29, 753; *Brit. Chem. Abs.* B, 1935, 773.

mole of aluminum chloride. The product is mixed with phenyl chloride to furnish a liquid having a melting point of —45°C. According to Austin[44] a *sec*-alkyl resorcinol may be secured from resorcinol and 1-chloro-2-methylheptane. The contact agent employed is zinc chloride and the temperature is maintained at 130°C. Koch[45] suggests that chlorinated paraffins boiling above 200°C. and from which the solid material has been removed be polymerized by heating to 130°C. in the presence of a Friedel-Crafts agent to furnish a synthetic lubricating oil. Also, it has been proposed that cracking and condensation of halogenated high-boiling oils be effected in the presence of aluminum which has been activated by treatment with mercuric chloride and hydrogen chloride.[46] In one instance, chlorine was conducted into a vessel containing a paraffin oil, the latter boiling above 350°C. (see Fig. 187). The reaction was begun at 20°C. and allowed to continue until an increase in weight of the oil of about 65 per cent had taken place. It was reported that the temperature rose to 100°C. at this point and that hydrogen chloride was split off. The halide was then admixed with an equal weight of an untreated gas oil boiling between 270 and 350°C. Nitrogen was incorporated as a diluent and the mixture led through a vessel containing the catalyst. During this step

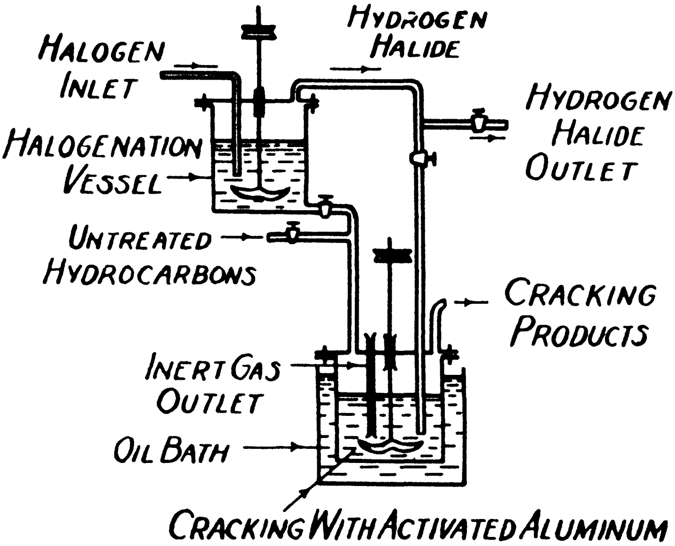

FIG. 187.—Halogenation and Cracking of High-Boiling Hydrocarbon Oils. (H. Engel and J. Jannek)

the temperature was maintained at 250°C. by means of an oil bath. In this manner, an oil was said to be secured, 40 per cent of which boiled below 200°C. and 15 per cent below 270°C. Fischer, Koch and Wiedeking[47] point out that polymerization of dichlorinated Kogasin[48] in the presence of aluminum chloride at 120°C. gives a synthetic oil which is said to have a high refractive index and to be resistant to oxidation. Resins may also be secured from petroleum distillates by this method. Fulton and Kunc[49] state that a petroleum distillate boiling between 150 and 350°C. under a pressure of 1 mm., may be chlorinated[50] and subjected to the action of a metal halide condensing agent. Thus, 1000 pounds of a distillate such as that mentioned above were chlorinated at 80°F. (26.6°C.). A cooling system was employed to maintain the temperature at that point until the chlorine content became 9.7 per cent by weight. The chlorinated products were then conducted into a vessel equipped with a reflux condenser and an agitator. There the halide was admixed with 50 pounds of anhydrous aluminum chloride and heated for 12 hours at 80-90°F. (26.6-32.3°C.). At the end of the heating period the products were washed and distilled. The highest boiling fraction was said to contain 293 pounds of a highly condensed product, which boiled off at 600°F. (315.5°C.) at 1 mm. The latter was ground and then extracted with 300 gallons

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[44] W. E. Austin, U. S. P. 2,006,039, June 25, 1935, to Redro Laboratories, Inc.; *Chem. Abs.*, 1935, **29**, 5602. U. S. P. 2,030,423, Feb. 11, 1936, to Bank of Manhattan Co.; *Chem. Abs.*, 1936, **30**, 2325. W. E. Austin, U. S. P. 2,023,160, Dec. 3, 1935; *Chem. Abs.*, 1936, **30**, 819. British P. 442,369, 1935; *Brit. Chem. Abs.* B, 1936, 443; *Chem. Abs.*, 1936, **30**, 4628. French P. 784,441, 1935; *Chem. Abs.*, 1936, **30**, 110.

[45] H. Koch, *Z. Ver. deut. Ing.*, 1936, 80, 49; *Chem. Abs.*, 1936, **30**, 2741.

[46] H. Engel and J. Jannek, U. S. P. 1,941,884, Jan. 2, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1850. British P. 417,659, 1934; *J. Inst. Pet. Tech.*, 1934, **20**, 618A; *Chem. Abs.*, 1935, **29**, 1242; *Brit. Chem. Abs.* B, 1935, 13.

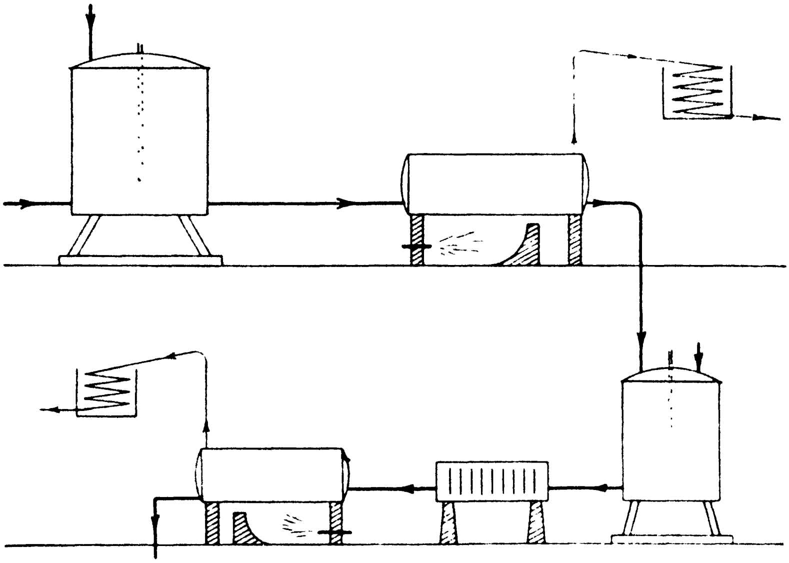

Fig. 188.—Flow Scheme for Resin Manufacture by Treatment of Chlorinated Distillates with Aluminum Chloride. (S. C. Fulton and J. Kunc)

of naphtha. After removing the solvent by distillation, 221 pounds of a resin with a softening point of 213°F. (100°C.) were reported to be obtained.[51]

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[47] F. Fischer, H. Koch and K. Wiedeking, *Brennstoff-Chem.*, 1934, 15, 229; *J. Inst. Pet. Tech.*, 1934, 20, 497A; *Brit. Chem. Abs.* B, 1934, 744; *Chem. Abs.*, 1934, 28, 6291.

[48] Hydrocarbon mixture made by the reaction of carbon monoxide and hydrogen. See Chapter 52.

[49] S. C. Fulton and J. Kunc, U. S. P. 2,038,558, Apr. 28, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, 30, 3093.

[50] The chlorination of petroleum hydrocarbons is described in Chapters 30 and 32.

Ulich and Heyne[52] have made a study of the kinetics of the reaction between benzene and propyl chloride in carbon disulphide solution. Chlorides of gallium and aluminum were employed as catalysts and the extent of alkylation was determined by measuring volumetrically the amount of hydrogen chloride evolved. It was found that with the first-mentioned contact agent the substitution of the propyl group proceeds by the formation of an intermediate, gallium chloride-propyl chloride complex. The latter is in equilibrium with the remainder of the condensing agent, the reactants and the product, propyl benzene. The rate of reaction may be expressed by the equation:

$$\frac{dv}{dt} = \frac{k[GaCl_3]\,[C_3H_7Cl]\,[C_6H_6]}{[C_6H_6] + K[C_3H_7Cl]}$$

where k = 750 and K = 0.5. With aluminum chloride the results agree partially with the above mechanism, but an additional factor is the formation of a complex of the product and catalyst.

A saturated Kogasin II having an average molecular formula of $C_{14}H_{30}$ may be chlorinated and then condensed with aromatics to furnish a species of lubricating oil.[53] Halogenation of the synthetic hydrocarbon mixture at room temperature (20°C.) yielded a composite of five products containing from 1 to 6 chlorine atoms per molecule. Reaction of the trichloro derivative with 1 to 3 volumes of xylene and 5 per cent by weight of aluminum chloride gave a 75 per cent yield of alkylated aromatic hydrocarbons. A material for increasing the viscosity of lubricating oils is secured by the condensation of benzene and ethylene dichloride. The reactants are heated to 40°C. with a Friedel-Crafts condensing agent and distilled to purify the substituted hydrocarbon. Condensation at 70-80°C. gives a viscous liquid suggested for increasing the transparency and adherent properties of paraffin wax.[54] Shinkle, Brooks and Cady[55] report that a plastic material obtained from this reaction at 110°C. finds application as a compounding agent for natural and synthetic rubber. According to Moran,[56] benzene and ethylene chloride begin to combine spontaneously when placed with aluminum chloride in a porcelain-lined kettle. The temperature should be held at 40-50°C. for 24 hours and then raised to 60-70°C. for 10 minutes and cooled again to 50°C. A few minutes after the temperature is lowered the mass will swell to about three times its original volume, forming a plastic material. Dichloroethane and benzene may also be united with oleic acid by the Friedel-Crafts synthesis.

Also, Ulich and Heyne[57] have investigated the speed of the condensation of benzoyl chloride and benzene in carbon disulphide solution, using gallium and aluminum chlorides as condensing agents. The extent of arylation was determined by measuring the volume of hydrogen chloride evolved. Condensation may be represented as:

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[51] For a discussion of the preparation of resins from chlorinated hydrocarbons by treatment with aluminum chloride, see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**.

[52] H. Ulich and G. Heyne, *Z. Elektrochem.*, 1935, 41, 509; ***Brit. Chem. Abs.* A**, 1935, 1207; ***Chem. Abs.***, 1935, **29**, 7768.

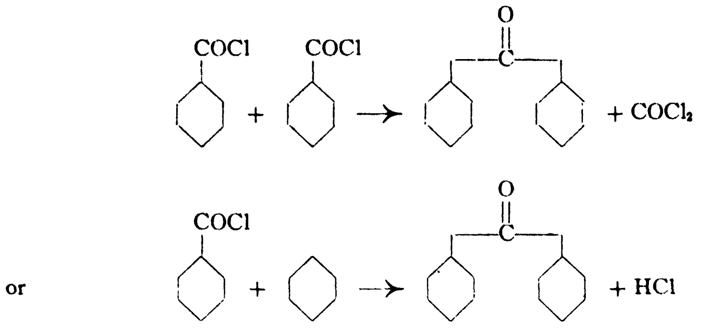
[53] F. Fischer and H. Koch, *Brennstoff-Chem.*, 1933, **14**, 463; *J. Inst. Pet. Tech.*, 1934, **20**, 102A; ***Chem. Abs.***, 1934, **28**, 2513; *Brit. Chem. Abs.* **B**, 1934, 1933.

[54] British P. 428,410, 1935, to Standard Oil Development Co.; ***Chem. Abs.***, 1935, **29**, 7062; ***Brit. Chem. Abs.* B**, 1935, 617; *J. Inst. Pet. Tech.*, 1935, **21**, 269A.

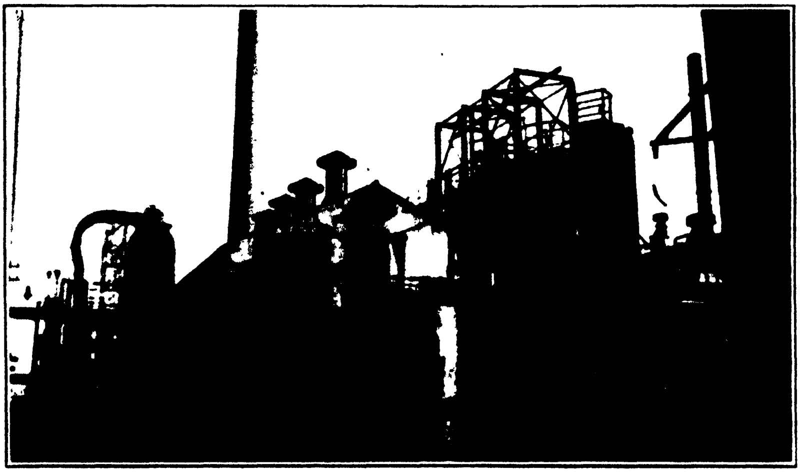
[55] S. D. Shinkle, A. E. Brooks and G. H. Cady, ***Ind. Eng. Chem.***, 1936, **28**, 275; ***Chem. Abs.***, 1936, **30**, 4233.

[56] R. C. Moran, U. S. P. 2,043,836, June 9, 1936, to Socony-Vacuum Oil Co.; ***Chem. Abs.***, 1936, **30**, 5406.

[57] H. Ulich and G. Heyne, *Z. Elektrochem.*, 1935, 41, 509; ***Chem. Abs.***, 1935, **29**, 7768; ***Brit. Chem. Abs.* A**, 1935, 1207.



With equimolecular proportions of benzoyl chloride and catalyst the reaction is unimolecular but does not go to completion because of the formation of a complex between benzophenone and the contact agent resulting in deactivation of the latter.



Courtesy Standard Oil Development Co.

FIG. 189.—Plant for Manufacture of Paraflow.

Trichlorodiphenylmethane is suggested as a transformer oil, one of its reported properties being non-inflammability. It may be prepared by condensing trichlorobenzyl chloride with an excess of benzene using aluminum chloride as a promoter.[58] Barbier[59] reports that the Friedel-Crafts synthesis may be utilized to convert *p-ter*-butyltoluene to an isopropyl-4-*ter*-butyltoluene by adding isopropyl chloride to the former. Transformation of phthalic anhydride to phthalyl chloride by treatment with benzotrichloride and a condensing agent has been proposed.[60] Reaction in the liquid phase at a temperature of 60° C. with zinc chloride as catalyst is said to give 95 per cent of the theoretical yield.

Condensation of halogenated heavy hydrocarbon material such as chlorinated paraffin wax, petrolatum or paraffin oil with aromatic hydrocarbons, e.g., naphthalene, gives products adaptable as pour point suppressors for lubricating oils.[61] In one process, 100 g. of a chlorinated wax are admixed with 10 g. of naphthalene and placed in a reaction chamber. The latter is equipped with a steam coil, agitator and a swiveled pipe which is designed to facilitate removal of the reaction products. The mixture of halide and aromatic is heated to 130-140°F. and 10 g. of aluminum chloride slowly incorporated. The reaction chamber is maintained at the above temperature for a period of 1 hour after the aluminum halide has been added. At the end of this time, carbon tetrachloride is employed to extract the condensed products which comprise the upper layer. These may then be drawn off through the swiveled pipe. A synthetic lubricating oil said to be free of resinous material has been formed by condensation of chlorinated paraffin wax with biphenyl.[62] Thus, 5 g. of biphenyl and 15 g. of aluminum chloride were dissolved in 200 g. of naphtha and the solution heated to 130-140°F. (55-60°C.). The chlorinated wax was then incorporated gradually into the solution and the mixture allowed to stand for a period of 2 hours. At the end of that time, the aluminum chloride was separated from the oily layer and the latter distilled to remove naphtha. In this

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[58] British P. 433,072, 1935, to British Thomson-Houston Co. Ltd.; *Brit. Chem. Abs.* B, 1935, 939; *Chem. Abs.*, 1936, 30, 489.

[59] H. Barbier, *Rev. Marques Parfum. Savonn*, 1934, 12, 325; *Brit. Chem. Abs.* A, 1936, 196.

[60] L. P. Kyrides, German P. 621,912, 1935; *Chem. Abs.*, 1936, 30, 2206.

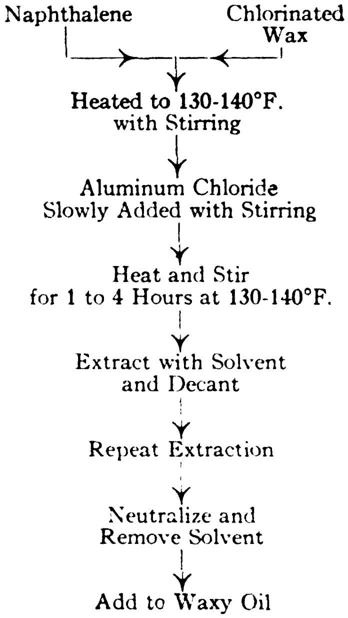
Naphthalene
Chlorinated Wax
Heated to 130-140°F. with Stirring
Aluminum Chloride Slowly Added with Stirring
Heat and Stir for 1 to 4 Hours at 130-140°F.
Extract with Solvent and Decant
Repeat Extraction
Neutralize and Remove Solvent
Add to Waxy Oil

FIG. 190.
Flow Diagram for Production of Pour-Point Depressor from Chlorinated Paraffin Wax. (F. H. MacLaren)

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[61] For a discussion of "Paraflow," see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. See K. S. Ramayya and S. Khaiman, *Neft. Khoz.*, 1934, **26** (12), 37; *Brit. Chem. Abs.* **B**, 1936, 356; *Chem. Abs.*, 1935, **29**, 4928. British P. 415,526, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1934, 1002; *Chem. Abs.*, 1935, **29**, 920. J. A. Anderson, U. S. P. 1,998,648, April 23, 1935, and C. E. Adams, U. S. P. 1,998,747, April 23, 1935, both to Standard Oil Co. of Ind.; *Brit. Chem. Abs.* **B**, 1936, 439; *Chem. Abs.*, 1935, **29**, 3821 and 3822. F. H. MacLaren, U. S. P. 1,963,917 and 1,963,918, June 19, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1934, **28**, 5226; *Brit. Chem. Abs.* **B**, 1935, 346. *Cf.* O. M. Reiff, U. S. P. 2,061,008, Nov. 17, 1936, to Socony-Vacuum Oil Co.; *Chem. Abs.*, 1937, **31**, 848. Y. Tanaka and R. Kobayashi, *J. Soc. Chem. Ind., Japan*, 1936, **39**, Suppl. binding 199; *Chem. Abs.*, 1936, **30**, 6545; *Brit. Chem. Abs.* **B**, 1936, 1029. British P. 458,105, 1936; *J. Inst. Pet. Tech.*, 1937, **23**, 76A; *Brit. Chem. Abs.* **B**, 1937, 115.

[62] F. H. MacLaren, U. S. P. 2,030,832, Feb. 11, 1936, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1936, **30**, 2365.

manner, a yield of 84 per cent of a light-colored oil, which is not susceptible to large viscosity changes with variations in temperature, was said to be secured.

Alkyl groups may be substituted in phenols by employing any of the agents specified for the Friedel-Crafts reaction (aluminum, ferric or zinc chloride). For example, Seymour[63] treated phenol with *ter*-butyl chloride at 80-90°C. in the presence of hydrated ferric chloride to obtain mainly *ter*-butylphenol. To obviate separation of unchanged butyl chloride from the hydrogen chloride leaving the reaction zone the mixed vapors may be passed into tertiary butyl alcohol, thus converting the hydrogen chloride into additional butyl halide.[64] *ter*-Butylphenolic compounds have been recommended as germicides, fungicides and preservatives[65] and also for the preparation of oil-soluble resins by condensation with aldehydes.[66] A highly alkylated aromatic ether resembling a lubricating oil and reported to have many properties of the latter has been produced from a chlorinated paraffin (containing 17 per cent of chlorine) and diphenyl ether.[67] Condensation is effected at 60°C. with a small portion of a Friedel-Crafts agent. Reichstein, Rosenburg and Eberhardt[68] report that methyl pyromucate reacts with *ter*-amyl chloride, when aluminum chloride is present, to furnish 5-*ter*-amylfuran-2-carboxylic acid, according to the equation,

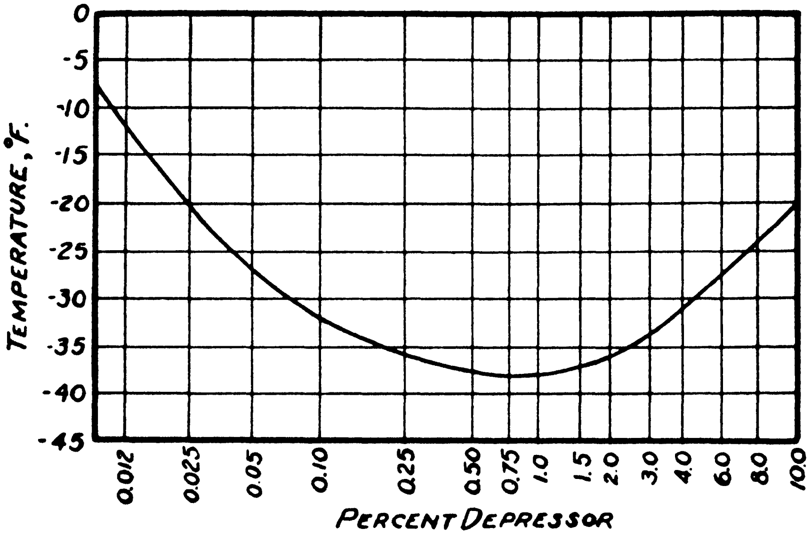

FIG. 191.—Effect of Depressor on Pour Point of Lubricating Oil. (F. H. MacLaren)

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[63] G. W. Seymour, U. S. P. 1,972,956, Sept. 11, 1934, to Celanese Corp. of America; *Chem. Abs.*, 1934, **28**, 6725. Canadian P. 340,996, 1934, to C. Dreyfus; *Chem. Abs.*, 1934, **28**, 4068. British P. 409,131, 1933, to British Celanese Ltd.; *Brit. Chem. Abs.* B, 1934, 535; *Chem. Abs.*, 1934, **28**, 6158.

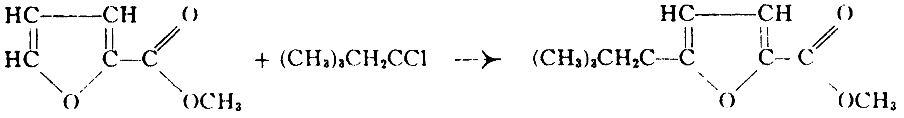
[64] R. P. Perkins, A. J. Dietzler and J. T. Lundquist, U. S. P. 1,991,332, Feb. 12, 1935, to Dow Chemical Co.; *Brit. Chem. Abs.* B, 1936, 91; *Chem. Abs.*, 1935, **29**, 2180.

[65] R. P. Perkins, A. J. Dietzler and J. T. Lundquist, U. S. P. 1,972,599, Sept. 4, 1934, to Dow Chemical Co.; *Chem. Abs.*, 1934, **28**, 6532; *Brit. Chem. Abs.* B, 1935, 716.

[66] Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935, Chapter 19.

[67] British P. 440,916, 1936, to Resinous Products and Chemical Co.; *Brit. Chem. Abs.* B, 1936, 261; *Chem. Abs.*, 1936, **30**, 4314; *J. Inst. Pet. Tech.*, 1936, **22**, 160A.

[68] T. Reichstein, H. R. Rosenburg and R. Eberhardt, *Helv. Chim. Acta*, 1935, **18**, 721; *Brit. Chem. Abs.* A, 1935, 1128; *Chem. Abs.*, 1935, **29**, 6232.



The latter compound, which boils at 108-110°C. under 11 mm. pressure, may be oxidized by potassium permanganate to dimethylethyl acetic acid.

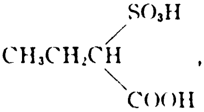
REACTION OF HALIDES OF PARAFFINS AND CYCLOPARAFFINS WITH SULPHITES

The reaction of aliphatic halides with aqueous solutions of sulphites is known as the Strecker reaction. For example, ethyl iodide will combine with sodium sulphite to give sodium iodide and sodium ethyl sulphonate.[69]

$$C_2H_5I + Na_2SO_3 \longrightarrow NaI + C_2H_5SO_3Na$$

Hemilian[70] reported that when ammonium sulphite is employed for this double displacement, the end of the reaction is very definitely marked.

$$RCl + (NH_4)_2SO_3 \rightleftharpoons NH_4Cl + R{-}NH_4SO_3$$

From the latter compound the acid may be obtained by boiling with lead dioxide and subsequently acidifying the lead salt. The method was used to prepare α-sulphobutyric acid,  $CH_3CH_2CH(SO_3H)COOH$, from the corresponding bromo compound and β-sulphobutyric acid,

$$CH_3 \cdot CHSO_3HCH_2COOH$$

from the chloro compound. In the same manner Wagner and Reid[71] synthesized a number of aliphatic sulphonic acids containing from 1 to 6 carbon atoms. Sulphonic acids did not result in the case of *sec*-amyl, *n*-hexyl, *sec*-hexyl and phenyl halides, though with halides of lower carbon content some sulphonic acids were obtained.

The above general reaction has been employed in making sulphonic acids from low-molecular-weight polyhalogenated hydrocarbons. In one process methylene iodide and aqueous sodium sulphite are allowed to interact at a temperature of 70°C., furnishing a 95 per cent yield of sodium iodomethane sulphonate.[72] Aurisicchio[73] employed triiodomethane instead of the dihalide. The reaction is carried out under reflux for a period of 5 hours at 70°C. The sodium iodide formed is decomposed by a stream of chlorine. Carbon dioxide is passed in to displace residual chlorine, and after removal of water ethyl alcohol is added to throw out the sulphonate. Use of copper as a contact agent and maintenance of a temperature of 120-140°C. in this reaction have also been recommended.[74] According to Lauer and Langkammerer[75] 0.6 mole of potassium sulphite mixed with 0.2 mole of triiodomethane and refluxed for 4 hours at 70°C. furnishes 73 per cent of the theoretical yield of potassium iodomethane sulphonate. Further treatment of the latter compound with potassium sulphite gives potassium methionate, $CH_2(SO_3K)_2$. The formation of β,β-disulphopropionic acid from potassium α,β-dibromoproprionate and potassium sulphite has been described by Backer and Beute.[76] Potassium α-bromo-β-sulphopropionate is first produced and splits off hydrogen bromide to become potassium β-sulphoacrylate. Further reaction of the latter with potassium sulphite yields β,β-disulphopropionic acid (potassium salt).

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[69] A. Strecker, *Ann.*, 1868, **148**, 92.

[70] W. Hemilian, *Ber.*, 1873, **6**, 562; *J.C.S.*, 1873, **26**, 1021.

[71] F. C. Wagner and E. E. Reid, *J.A.C.S.*, 1931, **53**, 3407; *Chem. Abs.*, 1931, **25**, 5393; *Brit. Chem. Abs.* **A**, 1931, 1268.

[72] British P. 353,477, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1931, 1132.

[73] G. Aurisicchio, *L'Ind. Chimica*, 1932, **7**, 714; *Brit. Chem. Abs.* **A**, 1932, 929; *Chem. Abs.*, 1933, **27**, 2420.

[74] British P. 369,473, 1930, to Soteria Chemische Fabrik A.-G.; *Brit. Chem. Abs.* **B**, 1932, 670; *Chem. Abs.*, 1933, **27**, 2161.

[75] W. M. Lauer and C. M. Langkammerer, *J.A.C.S.*, 1935, **57**, 2360; *Chem. Abs.*, 1936, **30**, 1737; *Brit. Chem. Abs.* **A**, 1936, 316.

$$CH_2Br{-}CHBr{-}COOK + K_2SO_3 \longrightarrow KO_3S{-}CH_2{-}CHBr{-}COOK \longrightarrow$$
$$KO_3S{-}CH{=}CH{-}COOK \longrightarrow (KO_3S)_2CH{-}CH_2{-}COOK$$

A number of alkane disulphonates in which the sulphonate groups are attached to the terminal carbon atoms have been prepared by Stone.[77] Alkane dibromides of the general formula $Br(CH_2)_nBr$ were reacted with sodium sulphite.

$$Br(CH_2)_nBr + 2Na_2SO_3 \longrightarrow NaO_3S(CH_2)_nSO_3Na + 2NaBr$$

One mole of the dibromide was added to an aqueous solution of 2.5 moles of sodium sulphite preheated to 100°C. The reaction time varied from 12 hours to 7 days. Aliphatic compounds containing more than 6 carbon atoms in a straight chain, with one halogen and one hydroxyl group on opposite terminal atoms, may be employed to produce a sulphonate by the Strecker reaction.[78] For example, 6-chloro-1-hexanol is converted to 6-hydroxyhexane-1-sulphonic acid by reaction with sodium sulphite at 170-180°C. The hydroxyl group may then be esterified with octoic or *n*-decylic acid. Reed and Tartar[79] report that the sulphonates of paraffins containing a large number of carbon atoms may be obtained by heating 1 mole of the corresponding alkyl bromide with 1.15 moles of aqueous sodium sulphite in an autoclave for a period of 9 hours at 180-200°C. After reaction the solution is evaporated to dryness and extracted with petroleum ether. In this manner the *n*-octyl, *n*-decyl, lauryl, myristyl, cetyl and *n*-octadecyl sulphonates were secured.

It is interesting to note that the Strecker reaction may be used with unsaturated halides in some cases. α-Sulphoacrylic acid is prepared from ammonium α-bromoacrylate, *cis* and *trans*-β-sulphoacrylic acid from β-chloroacrylic acid, and β-sulphocrotonic acid from ammonium β-chlorocrotonate, all by treatment with ammonium sulphite.[80]

Backer[81] states that diethyl ether-2,2′-dichloride reacts with ammonium sulphite to give diethyl ether-2,2′-disulphonic acid.

$$ClCH_2CH_2{-}O{-}CH_2CH_2Cl + (NH_4)_2SO_3 \longrightarrow H_4NO_3SCH_2CH_2{-}O{-}CH_2CH_2SO_3NH_4$$

The latter may be heated to 55°C. at 1 atmosphere pressure and treated with hydroxylamine (NH_2OH), yielding aminoalkylsulphonic acids.[82] Schindhelm and Bayer[83] point out that sodium sulphite replaces chlorine in 2-chlorobenzothiazole at 100°C. to furnish benzothiazole-2-sulphonic acid. 2-Chlorobenzoxazole is similarly converted to benzoxazole-2-sulphonic acid.

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[76] H. J. Backer and A. E. Beute, *Rec. trav. chim.*, 1935, **44**, 601; *Brit. Chem. Abs.* **A**, 1935, **1106**.

[77] G. C. H. Stone, *J.A.C.S.*, 1936, **58**, 488; *Brit. Chem. Abs.* **A**, 1936, 589; *Chem. Abs.*, 1936, **30**, 2918.

[78] British P. 444,239, 1936, to Deutsche Hydrierwerke A.-G.; *Chem. Abs.*, 1936, **30**, 5594; *J. Inst. Pet. Tech.*, 1936, **22**, 272A.

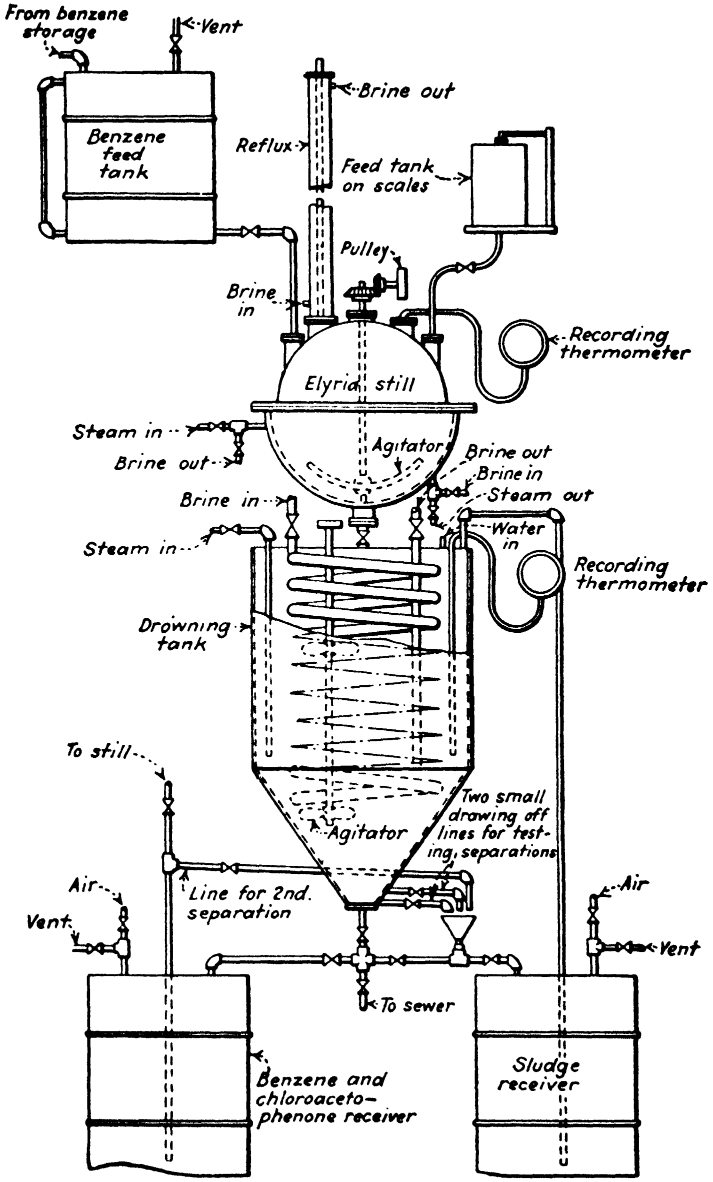
[79] R. M. Reed and H. V. Tartar, *J.A.C.S.*, 1935, **57**, 570; *Brit. Chem. Abs.* **A**, 1935, 606; *Chem. Abs.*, 1935, **29**, 2915. A. Davidson, U. S. P. 2,053,424, Sept. 8, 1936, to Imperial Chemical Industries Ltd.; *Chem. Abs.*, 1936, **30**, 7125.

[80] H. J. Backer and A. E. Beute, *Rec. trav. chim.*, 1935, **54**, 200, 523, 551; *Brit. Chem. Abs.* **A**, 1935, 476, 961; *Chem. Abs.*, 1935, **29**, 5817, 2913.

[81] H. J. Backer, *Rec. trav. chim.*, 1935, **54**, 205; *Chem. Abs.*, 1935, **29**, 2915; *Brit. Chem. Abs.* **A**, 1935, 472.

[82] British P. 446,829, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1936, 683.

[83] H. Schindhelm and O. Bayer, German P. 609,025 and 613,172, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 3174, 5459.



Courtesy McGraw-Hill Book Co., Inc.

FIG. 192.—Plant Assembly for Production of Aralkyl Ketones by Friedel-Crafts Reaction. (P. H. Groggins)

DOUBLE DECOMPOSITION OF SALTS OF INORGANIC ACIDS WITH ALKYL AND ARYL HALIDES

Alkyl halides undergo double decomposition with metallic cyanides to form nitriles which may then be oxidized to the corresponding acids.[84] For example, 1 mole of amyl chloride refluxed for 48 hours with 1.1 moles of sodium cyanide in a solvent of 80 per cent ethanol and 20 per cent water gave an 80 per cent yield of nitrile. However, when an equimolecular proportion of sodium iodide was added to the reaction chamber, the yield increased to 90 per cent. This was attributed to the formation of amyl iodide, which is more reactive than the chloride.

$$\begin{aligned} C_5H_{11}Cl + NaI &\longrightarrow C_5H_{11}I + NaCl \\ C_5H_{11}I + NaCN &\longrightarrow C_5H_{11}CN + NaI \end{aligned}$$

Rosenmund and Struck[85] stated that halogen atoms attached to the nucleus of an aromatic hydrocarbon can be replaced by the cyanide group if a mixture of potassium and cuprous cyanides is employed and the temperature maintained at 200°C. The formation of the aromatic nitrile was found to take place regardless of whether or not other substituents or other halogens were present on the nucleus. On the other hand Feist[86] points out that the replacement of chlorine in phenyl chloride by this method is tedious and the yield of benzoic acid low, and in the case of 1,2,4-trichlorobenzene and hexachlorobenzene no nitrile or acid is formed. Mellitic acid, $C_6(COOH)_6$, was secured, however, from tetrachlorophthalic acid by the above procedure.

The alkyl halides will also react with alkali hydrosulphides to yield mercaptans. Thus, ethyl chloride may be treated with sodium hydrosulphide to secure ethyl mercaptan. By condensing the latter with acetone in the presence of zinc chloride and subsequently oxidizing the mercaptol, sulphonal, a hypnotic drug, is obtained. Treatment of polychlorinated paraffins of higher carbon content than octane with an alcoholic solution of a hydrosulphide and subsequent mild oxidation with nitric acid is reported to yield emulsifying agents applicable in textile and pharmaceutical industries.[87] Reaction of aliphatic mercaptans with aliphatic compounds containing replaceable halogen gives aliphatic sulphides, those of high molecular weight having a soapy character.[88] In this manner the sodium salts of α-(ethylmercapto)-stearic acid, dodecylmercaptoacetic acid and dodecyl-β,γ-dihydroxypropyl sulphide have been prepared.

According to Salzberg and Bousquet[89] dodecyl chloride dissolved in ethanol and treated with sodium thiocyanate for 8 hours at 125°C. forms dodecyl thiocyanate which may be employed as an insecticide.

REACTIONS OF HALOGEN DERIVATIVES OF PARAFFINS AND CYCLOPARAFFINS WITH MAGNESIUM

When alkyl halides are treated in ether solution with magnesium, direct combination takes place with a resulting formation of magnesium alkyl halides classed with the Grignard reagents.[90] The same reaction occurs with some of the aromatic halides, though in certain cases a solvent is not required. The Grignard reagent has been employed to great extent in experimental work, especially in organic syntheses and in the qualitative determination of alkyl halides.[91] Industrial use is limited, however, because of the relatively high cost of magnesium and the difficulty of recovering the latter in a metallic state. However, in the preparation of lead tetraethyl (tetraethyl plumbane), ethyl magnesium chloride and lead bromide have been employed. The lead ethide has been utilized as an antiknock agent for internal combustion engines.[92] Other compounds of this type, but containing the diethylmethyl radical, have also been suggested as knock-suppressors. Thus dimethyl bis(diethylmethyl)lead can be prepared by adding diethylchloromethane and methyl iodide to a mixture of lead chloride, magnesium and ether.[93] In the procedure, 48 g. of metallic magnesium were placed in a glass reaction flask together with 277 g. of lead chloride. Diethyl ether (148 g.) was employed as a solvent for reaction products. A mixture of 106 g. of diethylchloromethane and 141 g. of methyl iodide were then incorporated dropwise in the mixture. At the end of a contact period of 1 hour, the reaction products were cooled to 0°C. Dilute hydrochloric acid was then added slowly to bring about a separation of the ether layer. The latter contained the dissolved dimethyl bis(diethylmethyl)lead.

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[84] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[85] K. W. Rosenmund and E. Struck, *Ber.*, 1919, **52**, 1749; *Chem. Abs.*, 1920, **14**, 1546; *J.S.C.I.*, 1920, **39**, 82A.

[86] F. Feist, *Ber.*, 1935, **68**, 1941; *Chem. Abs.*, 1936, **30**, 451; *Brit. Chem. Abs.* **A**, 1935, 1497.

[87] British P. 361,356 and 361,357, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, **27**, 1890; *Brit. Chem. Abs.* **B**, 1932, 93.

[88] French P. 748,460, 1933, to Henkel & Cie. G.m.b.H.; *Chem. Abs.*, 1933, **27**, 5340.

[89] P. L. Salzberg and E. W. Bousquet, Canadian P. 354,650, 1935, to Canadian Industries Ltd.; *Chem. Abs.*, 1936, **30**, 2325.

Materials advocated as disinfectants, insecticides or fungicides and also as antioxidants or paint driers may be prepared by heating a lead tetra-alkyl with a phenol in the presence of silica gel.[94] For example, 14.5 g. of phenol and 49 g. of lead tetraethyl were heated at 150-155°C. for 2.5 hours in the presence of 0.25 g. of silica gel. At the end of that time the reaction mixture was cooled to 20°C. and solidified. The solid material was recrystallized from benzene. In this manner 38 g. of triethyl lead phenolate, a yellow powder which decomposes at 205°C., were said to be obtained.

In an analysis of a mixture of alkyl chlorides, it has been found advantageous to convert the chloride to the corresponding anilide and determine the melting point of that substance.[95] The reason for this step is that the anilides of isomers of the alkyl chlorides have sharply defined melting points which differ from each other.[96] To secure the anilide, the chloride is first converted into the corresponding Grignard compound which is then treated with phenyl isocyanate, C_6H_5NCO. In some cases the toluides and α-naphthylamides are also useful for the same purpose. The melting points of some of the anilides are given in Table 169.

Although at 5 to 15°C. butyl and isoamyl chloride react with magnesium to form a Grignard compound, use of higher temperatures (78 and 99°C., respectively) results in violent reaction producing olefins, paraffins and magnesium chloride, according to the equation[97]

$$2C_nH_{(2n+1)}Cl + Mg \longrightarrow MgCl_2 + C_nH_{2n} + C_nH_{2n+2}$$

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[90] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[91] For a review of uses of Grignard reagents in various syntheses, see A. D. Petrov, *Uspekhi Khim.*, 1934, **3**, 1050; *Chem. Abs.*, 1935, **29**, 6203.

[92] This is discussed in Chapter 44. For the determination of lead tetraethyl, see J. Studinger, *Chem and Ind.*, **1937**, 235.

[93] G. Alleman, U. S. P. 1,949,948 and 1,949,949, March 6, 1934, to Sun Oil Co.; *Brit. Chem. Abs.* **B**, 1935, 93; *Chem. Abs.*, 1934, **28**, 3229.

[94] W. H. Carothers, U. S. P. 2,008,003, July 16, 1935, to E. I. du Pont de Nemours & Co.; *Chem Abs.*, 1935, **29**, 5862.

[95] See Chapter 30.

[96] H. W. Underwood, Jr. and J. C. Gale, *J.A.C.S.*, 1934, **56**, 2117; *Brit. Chem. Abs.* **A**, 1934, 1330; *Chem. Abs.*, 1935, **29**, 115.

[97] P. P. Shoruigin, V. I. Isagulyantz and A. R. Guseva, *J. Gen. Chem.* (*U.S.S.R.*), 1934, **4**, 689; *Chem. Abs.*, 1935, **29**, 3660.

TABLE 169.—*Melting Points of Anilides Derived from Alkyl Chlorides.*

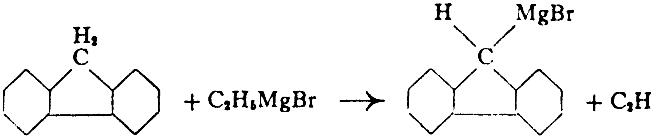
Chloride	B.P. of Chloride °C.	M.P. of Anilide °C.
Methyl	− 23.7	112-113
Ethyl	12.5	104-104.5
Isopropyl	36.5	104-104.5
n-Propyl	46.5	91-92
ter-Butyl	51	132-133
sec-Butyl	68	105.5-106.5
Isobutyl	68.5	109-110
n-Butyl	78	62-63
ter-Amyl	86	90-91
3-Chloropentane	96.7-97.1	126-127
2-Chloropentane	96-97	86-87
Isoamyl	99	110-110.5
n-Amyl	106	94-95

According to Flood and Calingaert[98] *ter*-butyl chloride and magnesium do not form an alkyl magnesium chloride. Instead, at 10-15°C., isobutene, isobutane and small proportions (10 per cent) of hexamethylethane, diisobutylene and higher polymers are secured.

Some alkyl bromides, also, do not lead to Grignard reagents when treated with magnesium. Ethylene bromide, for instance, is said to break down to ethylene and magnesium bromide dietherate [$MgBr_2$—$(C_2H_5)_2O$], if ether is employed as a solvent.[99] At most, a trace of ethylene magnesium bromide is found. 1,2,3-Tribromoisobutane when added to magnesium in ethereal solution also breaks down, furnishing diisobutenyl.[100]

$$2CH_3CBr(CH_2Br)_2 + Mg \longrightarrow [CH_2C({=}CH_2)CH_3]_2 + MgBr_2$$

As stated above, aromatic organo magnesium compounds may also be formed from the corresponding chlorides and in some cases a solvent is not required. Reaction of α-chloronaphthalene with magnesium (filings) at 200°C. is exothermic, with a reported yield of 16 per cent of naphthalene magnesium chloride.[101] Treatment of benzyl chloride in a similar manner furnished a resin whose structure was not determined. Miller and Bachman[102] report that magnesium suspended in ether readily combines with 9-bromo-phenanthrene to form an organo magnesium bromide in 92-93 per cent yield.[103] Fluorene also forms this compound by interaction with ethyl magnesium bromide in boiling xylene (144°C.) according to the equation,



The amount of 9-fluorylmagnesium bromide was estimated by measuring the volume of ethane evolved. Some of the results are indicated in Table 170.

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[98] D. T. Flood and G. Calingaert, *J.A.C.S.*, 1934, 56, 1211; *Chem. Abs.*, 1934, **28**, 4371; *J. Inst. Pet. Tech.*, 1934, **20**, 406A; *Brit. Chem. Abs.* **A**, 1934, 752.

[99] C. L. Tseng and F. M. Fam, *Science Quart. Natl. Univ. Peking*, 1934, **4**, 1; *Brit. Chem. Abs.* **A**, 1934, 508; *Chem. Abs.*, 1934, **28**, 4376.

[100] S. V. Lebedev and Ya. M. Slobodin, *J. Gen. Chem.* (*U.S.S.R.*), 1934, **4**, 23; *Brit. Chem. Abs.* **A**, 1934, 864; *Chem. Abs.*, 1934, **28**, 5399.

[101] P. P. Shoruigin, V. I. Isagulyantz and A. R. Guseva, *loc. cit.*

[102] H. F. Miller and G. B. Bachman, *J.A.C.S.*, 1935, **57**, 766; *J. Inst. Pet. Tech.*, 1935, **21**, 160A; *Chem. Abs.*, 1935, **29**, 3671; *Brit. Chem. Abs.* **A**, 1935, 741.

[103] H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, *J.A.C.S.*, 1923, **45**, 150; *Chem. Abs.*, 1923, **17**, 530; *J.S.C.I.*, 1923, **42**, 243A.

TABLE 170.—*Yield of 9-Fluorylmagnesium Bromide.*

Moles of C_2H_5MgBr	0.42	0.63	0.63
Moles of fluorene	.03	.05	.05
Hours of heating	12	18	66
Gas volume, cc. S.T.P.	201	345	364
Yield, per cent	30	30.8	32.5

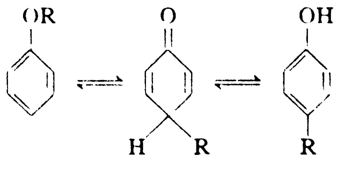
PRODUCTION OF ETHERS FROM CHLORINATED PARAFFINS

Alkyl and aralkyl halides condense with alkali alcoholates or phenolates to form ethers,

$$RX + NaOC_nH_{2n+1} \longrightarrow ROC_nH_{2n+1} + NaX$$
$$RX + NaOC_6H_5 \longrightarrow ROC_6H_5 + NaX$$

The second of these reactions seems to be effected more easily, and the aralkyl ethers obtained are said to be of industrial importance in dyeing.[104] Dispersing or emulsifying agents may be obtained by sulphonation of the ethers derived from chlorinated high-molecular-weight hydrocarbons. Similar treatment of phenoxy ethers derived from the same source furnishes leather solvents. A plastic material for molding compositions may be obtained from ethylene dichloride and sodium phenolate heated with ammonium carbonate at 160-190°C. for 6 hours.[105]

An alkyl ether of 1,2-dihydroxybenzene (pyrocatechol) may be prepared by treating the barium salt of the latter with methyl chloride.[106] Xylene is employed as an inert solvent and the temperature is maintained at 240°C. In a somewhat similar manner, a mixture of mono- and di-decyl ethers of a dihydroxy benzene may be secured.[106a]. Alkyl chlorides and alkali phenolates will also yield ethers.[107] For instance, ethyl alcohol is employed to dissolve 117 g. of sodium phenolate, to which is added 145 g. of diisobutyl chloride. The mixture is refluxed for 2 hours and the alcohol then evaporated. Water may be added to separate the salt and diisobutyl phenyl ether and the latter then washed with sodium hydroxide. The ether showed no evidence of rearrangement into a substituted phenol on being heated to 250°C. for 2 hours. In the case of *ter*-amyl and *ter*-butyl chloride, however, reaction of 1 mole of either of these substances with 1 mole of potassium phenolate at 75°C. leads to the corresponding phenyl ethers, but a rise in temperature to 125° C. for 2 hours, then to 180°C. for 1 hour, causes rearrangement to substituted phenols.



Employment of the latter as antiseptics and for the preparation of oil-soluble phenol-aldehyde resins has been suggested.[108] Some of the general rules for rearrangement given by Natelson follow:

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[104] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[105] C. F. Prutton, U. S. P. 1,950,516, March 13, 1934, to Dow Chemical Co.; *Chem. Abs.*, 1934, **28**, 3196; *Brit. Chem. Abs.* **B**, 1935, 111.

[106] K. Marx, H. Wesche, K. Bittner and H. Saenger, U. S. P. 2,024,534, Dec. 17, 1935, to General Aniline Works; *Chem. Abs.*, 1936, **30**, 1067.

[106a] J. H. Werntz, U. S. P. 2,067,960, Jan. 19, 1937, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, **31**, 1428.

[107] S. Natelson, *J.A.C.S.*, 1934, **56**, 1583; *Chem. Abs.*, 1934, **28**, 5052; *Brit. Chem. Abs.* **A**, 1934, 999.

[108] See Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

1. All alkyl or cyclohexyl phenyl ethers will form equilibrium mixtures of ether and substituted phenol at high temperatures (175-250°C.).
2. Increase in the molecular weight of the alkyl group favors production of substituted phenols.
3. If the ether-forming carbon of the alkyl group is tertiary, a greater percentage of substituted phenols will result than with a secondary or primary carbon atom.
4. A negative group attached to the ether-forming carbon shifts the equilibrium in favor of substituted phenol formation.
5. Substituting an alkyl group in the phenyl nucleus of an alkyl phenyl ether leads to increased amounts of ethers.
6. Equilibrium mixtures of ortho- and para-substituted phenols are obtained on rearrangement.

Vaughn, Vogt and Nieuwland[109] have studied the condensation of a number of alkyl halides with sodium alcoholates in a solution of liquid ammonia. The temperature was maintained between —33° and —10°C. and the pressure between 1 and 10 atmospheres. The chlorides were found to be almost unreactive. Bromides gave the highest yields of ethers, together with some olefins. Because of the formation of olefins, the iodides were not effective in bringing about large yields of ethers. Some of the results of this investigation are shown in Table 171.

TABLE 171.—*Yields of Ether from Alkyl Halides and Sodium Alcoholates.*

Sodium Derivative of	Alkyl Halide	Time Hours	Pressure Atm.	Product	Yield %
n-Propanol	Propyl bromide	1.5	1	Dipropyl ether	12
n-Butanol	Butyl bromide	1	1	Dibutyl ether	8
n-Butanol	Butyl bromide	1	10	Dibutyl ether	28
n-Pentanol	Amyl chloride	2	2.7	Diamyl ether	3
n-Pentanol	Amyl bromide	2-5	1.7-2.7	Diamyl ether	32-33
n-Pentanol	Amyl iodide	2	2.7	Diamyl ether	17
n-Pentanol	Butyl chloride	2	3	Amyl butyl ether	0
n-Pentanol	Butyl bromide	2	3	Amyl butyl ether	28

Ethyl sorbitol ether has been obtained by reaction of ethyl chloride with sorbitol in aqueous alkaline solution, treatment taking place in a nickel autoclave at 140-155°C. for 5 hours.[110]

It is interesting to note that aralkyl halides will also condense with alcohol to form ethers. According to Nixon and Brauch[111] the reaction of triphenylmethyl chloride in an excess of alcohol is a unimolecular mechanism, with the reaction-rate constant proportional to the initial concentration of the halide. The energy of activation of triphenylmethyl chloride is reported to be 13,420 cal. per mole.

The reaction of alkyl and aryl halides with sodium leads to the formation of free radicals, though in the case of the aryl radicals there seems to be some disagreement as to their nature. The reaction between sodium vapor and methyl or ethyl bromide is said to proceed according to the equation,[112]

$$\mathrm{Na} + \mathrm{RBr} \rightleftharpoons \mathrm{NaBr} + \mathrm{R}$$

The presence of free radicals at a distance of 8 cm. from the point of formation was detected by reacting the radicals with chlorine and iodine. Horn and

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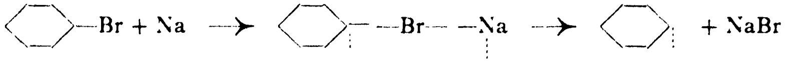
[109] T. H. Vaughn, R. R. Vogt and J. A. Nieuwland, *J.A.C.S.*, 1935, 57, 510; *Brit. Chem. Abs.* **A**, 1935, 605; *Chem. Abs.*, 1935, **29**, 2908.

[110] W. E. Lawson, U. S. P. 1,936,093, Nov. 21, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 778; *Brit. Chem. Abs.* **B**, 1934, 824.

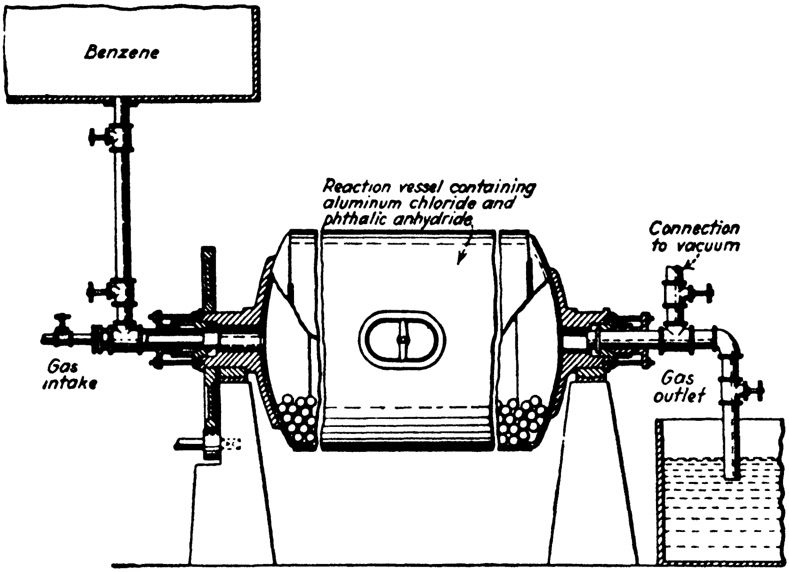
[111] A. C. Nixon and G. E. K. Brauch, *J.A.C.S.*, 1936, **58**, 492; *Chem. Abs.*, 1936, **30**, 3303.

[112] E. Horn, M. Palanyi and D. W. G. Style, *Z. physik. Chem.*, 1933, **B23**, 291; *Chem. Abs.*, 1934, **28**, 1013; *Brit. Chem. Abs.* **A**, 1933, 1269.

Polanyi[113] report that the action of sodium vapor on bromobenzene gives gaseous phenyl. On the other hand, Morton and Stevens[114] hold that there is an intermediate step in this reaction, the formation of a complex of bromobenzene and sodium, designated as a "metal halyl." The reaction was explained to be



Dotted lines represent partial valences, some of which serve to bind the phenyl radical and the sodium to the polar atom, and others which are unsaturated and represent unused combining power. As may be seen from the above course of reaction, the "metal halyl" eventually becomes a free phenyl radical. Also, it has been stated that sodium promotes reaction between aromatic hydrocarbons and alkyl halides which in its absence would be relatively inert to each other. For example, 100 g. of anthracene may be dissolved in 500 cc. of diethyl ether and 35 g. of powdered sodium added. Treatment with 165 g. of isoamyl chloride gives 9,10-diisoamyl-9,10-dihydroanthracene.[115] An analogous reaction takes place in the case of phenanthrene and isobutyl chloride, dihydrodiisobutylphenanthrene being obtained.[116]


Benzene
Reaction vessel containing aluminum chloride and phthalic anhydride
Connection to vacuum
Gas intake
Gas outlet

Courtesy McGraw Hill Book Co., Inc.

FIG. 193.—Mill-Type Reactor for Friedel-Crafts Syntheses. (P. H. Groggins)

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[113] E. Horn and M. Polanyi, *Z. physik. Chem.*, 1934, **B25**, 151; *Brit. Chem. Abs.* **A**, 1934, 641; *Chem. Abs.*, 1934, **28**, 4390.

[114] A. A. Morton and J. R. Stevens, *J.A.C.S.*, 1932, **54**, 1919; *Brit. Chem. Abs.* **A**, 1932, 728; *Chem. Abs.*, 1932, **26**, 3249. *J.A.C.S.*, 1931, **53**, 2244; *Brit. Chem. Abs.* **A**, 1931, 1050; *Chem. Abs.*, 1931, **25**, 3643. *J.A.C.S.*, 1931, **53**, 2769; *Chem. Abs.*, 1931, **25**, 4248; *Brit. Chem. Abs.* **A**, 1931, 1058. *J.A.C.S.*, 1931, **53**, 4028; *Chem. Abs.*, 1932, **26**, 122; *Brit. Chem. Abs.* **A**, 1932, 157. A. A. Morton, W. J. LeFevre and I. Hechenbleikner, *J.A.C.S.*, 1936, **58**, 754; *Chem. Abs.*, 1936, **30**, 4841. A. A. Morton and I. Hechenbleikner, *J.A.C.S.*, 1936, **58**, 1024; *Chem. Abs.*, 1936, **30**, 5185. *J.A.C.S.*, 1936, **58**, 1697; *Chem. Abs.*, 1936, **30**, 7535. *J.A.C.S.*, 1936, **58**, 2599; *Chem. Abs.*, 1937, **31**, 671.

[115] M. Lerer, *Ann. combustibles liquides*, 1935, **10**, 455; *J. Inst. Pet. Tech.*, 1935, **21**, 336A; *Chem. Abs.*, 1935, **29**, 6593.

[116] G. Hugel and M. Lerer, *Bull. soc. chim.*, 1933, **53**, 1502; *Chem. Abs.*, 1934, **28**, 4055; *Brit. Chem. Abs.* **A**, 1934, 642.

In the manufacture of sulphide plastics, alkyl halides and caustic soda may be employed. In a process described by Ellis,[117] aqueous caustic soda is mixed with sulphur and refluxed to dissolve the latter. Methanol, ethylene chloride and formaldehyde are added to the sodium polysulphide and the composite is heated to 80°C. for several hours, then cooled gradually. A resinous plastic which is said to have strong coherence and which may be drawn into threads or sheets results The above type of reaction in the presence of copper sulphate is reported to furnish an unsaturated hydroxylated hydrocarbon suggested as a lubricant.[118] Thus, 115 g. of chlorinated paraffin containing 3 chlorine atoms per molecule and having a molecular weight of 367 were admixed with 225 g. of aqueous caustic soda and 5 g. of copper sulphate. The reaction was effected in an autoclave by heating to 220-225°C. for 16 hours. Hydrochloric acid was then added to the products until the latter showed an acid reaction, at which point an oil layer was said to be formed. The latter was reported to contain 88 g. of a light brown oil, having 1 chlorine atom per molecule. In one method, chloroethylether, instead of ethylene chloride, is a reactant.[119] Caustic soda, magnesium chloride and sodium polysulphide in aqueous solution are heated with 2,2′-dichloroethyl ether. The condensation product obtained may be employed in vulcanizing rubber.

Hydrolysis of methyl(chlorophenyl)chloromethane with aqueous caustic soda and subsequent treatment with concentrated sulphuric acid to dehydrate the methyl (chlorophenyl)carbinol is suggested for the production of chlorostyrene.[120] The equations for the procedure are

$$ClC_6H_4CHClCH_3 \xrightarrow{NaOH} ClC_6H_4CHOHCH_3 \xrightarrow{H_2SO_4} ClC_6H_4CH{=}CH_2$$

Methylenepyrocatechol may be secured in 20 per cent yield from this phenol, potassium hydroxide and methylene chloride.[121] The method consists of heating a suspension of 50 g. of pyrocatechol, 40 g. of potassium hydroxide and 140 g. of methylene chloride in 200 cc. of water. The reaction chamber is an autoclave in which a temperature of 120°C. is maintained during the time of contact, 24 hours. The following properties are reported for methylenepyrocatechol:

Boiling point (11 mm.) 57°C.
d^{20}_{20} 1.185 n^{20}_{D} 1.53867

Trichloromethyl-*p*-chlorophenylcarbinol and the corresponding tribromo compound have been obtained by addition of chloroform and bromoform to *p*-chlorobenzaldehyde.[122] The trichloromethyl compound boiled at 187-188°C. under 26 mm. pressure, and the tribromo derivative had a melting point of 90-91°C. Dehalogenation of alkyl halides furnishes a means of obtaining pure hydrocarbons. For example, to obtain heptane, 179 g. of heptyl bromide are heated with 400 g. of zinc and 500 cc. of ethyl alcohol at 78°C. for 12 hours.[123] At the end of that period the mixture is distilled and refluxed with potassium hydroxide, the oily layer separated and again distilled. The yield is said to be 79 per cent.

Alkyl halides undergo double decomposition when treated with thiosulphate salts, furnishing, in the case of the monohalides, substances which are said to be effective as emulsifying agents and as plastics in the case of dihalides. In one procedure, *n*-dodecyl iodide and ammonium thiosulphate are heated to 78°C. in an ethanol solvent to obtain *n*-dodecyl ammonium thiosulphate, which is used as a soap.[124] Twiss and Neale[125] have prepared sulphides reported to be applicable in increasing the oil-resistant properties of rubber. Ethylene chloride was caused to interact with sodium thiosulphate in aqueous ethanol at 75°C. The alkene thiosulphate was then acidified by acetic acid and heated with hydrogen peroxide.

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[117] Carleton Ellis, U. S. P. 1,964,725, July 3, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1934, **28**, 5264; *Brit. Chem. Abs.* B, 1935, 368.

[118] K. Keller and E. Gofferje, U. S. P. 1,968,151, July 31, 1934, to General Aniline Works; *Chem. Abs.*, 1934, **28**, 5998.

[119] British P. 438,965, 1935, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1936, 161; *Chem. Abs.*, 1936, **30**, 3131. French P. 779,927, 1935; *Chem. Abs.*, 1935, **29**, 5548.

[120] Yu. Zal'kind, M. K. Amusin and I. P. Berkovich, Russian P. 38,630 and 38,638, 1935; *Chem. Abs.*, 1936, **30**, 3445, 3446.

[121] M. Mattier, *Arch. sci. phys. mat.*, 1935, 17, 289; *Chem. Abs.*, 1936, **30**, 443.

[122] J. W. Howard, *J.A.C.S.*, 1935, 57, 2317; *Brit. Chem. Abs.* A, 1936, 201.

[123] C. H. Kao and W. S. Chang, *J. Chinese Chem. Soc.*, 1934, 2, 18; *Brit. Chem. Abs.* A, 1934, 752; *Chem. Abs.*, 1934, **28**, 3711.

Acetylene carboxylic acids may be prepared from 1,2-dibromobutane and sodium amide.[126] The latter is mixed with kerosene and the dihalide incorporated at a temperature of 145°C. At the end of the reaction period (2.5 hours) the volume of the mixture is doubled by addition of a diluent such as ethyl ether. A stream of carbon dioxide is then conducted into the solution to form the ammonium salt of the acid which on treatment with hydrochloric acid yields ethyl propiolic acid ($CH_3CH_2C{\equiv}CCOOH$). Lesbre[127] points out that sodium plumbite and ethyl iodide react according to the equation:

$$Pb(ONa)_2 + C_2H_5I \longrightarrow C_2H_5PbOONa + NaI \xrightarrow{HOH} C_2H_5PbOOH$$

The resulting ethyl plumbonic acid is said to be amphoteric, amorphous and infusible.

In the manufacture of lead alkyls as antiknock agents for motor fuels several methods employ the reaction of alkyl halides with lead-sodium alloys.[128] To reduce hazards in large-scale production of lead tetraethyl it has been suggested that the alloy be first heated to 35-55°C. and then activated with a small proportion of ethyl chloride before the remainder of the latter is added to the reaction.[129] Voorhees[130] proposed to make lead compounds for knock suppression directly from gasoline. In the procedure a mixture of fused sodium chloride and lead was electrolyzed in a cell having an anode of graphite and a cathode of molten lead (see Fig. 194). In this manner a lead-sodium alloy was formed at the cathode, while chlorine was liberated at the anode. The latter vapor was employed to halogenate a gasoline fraction containing a small proportion of ethane. The chlorinated gasoline and lead-sodium were then conducted into a reaction vessel. A portion of the halogenated hydrocarbon was first vaporized to aid in atomizing the alloy. When the two substances were admixed, lead tetra-alkyls were said to be formed in the gasoline. In this manner, the danger of industrial poisoning from lead tetraethyl was said to be reduced.

Chloroethanes, on treatment with sulphuric acid, lead to sulphates and carboxylic acids. To obtain glyoxal sulphate, tetrachloroethane is heated to 55-60°C. and reacted with fuming sulphuric acid containing 65 per cent of sulphur trioxide, using a catalyst of mercuric sulphate. On cooling the mixture the glyoxal sulphate crystallizes and may then be filtered, washed with sulphuric acid and ice water and dried.[131] The formation of the sulphate may be expressed by the equation,

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[124] British P. 417,930, 1934, to Henkel & Cie. G.m.b.H.; *Brit. Chem. Abs.* **B**, 1935, 13; *Chem. Abs.*, 1935, **29**, 1433. French P. 765,360, 1934; *Chem. Abs.*, 1934, **28**, 6958. For a discussion of the kinetics of such reactions, see E. A. Moelwyn-Hughes, *J.C.S.*, **1933**, 1576; *Chem. Abs.*, 1934, **28**, 1594; *Brit. Chem. Abs.* **A**, 1934, 152.

[125] D. F. Twiss and A. E. T. Neale, British P. 412,349, 1934, to Dunlop Rubber Co.; *Brit. Chem. Abs.* **B**, 1934, 751.

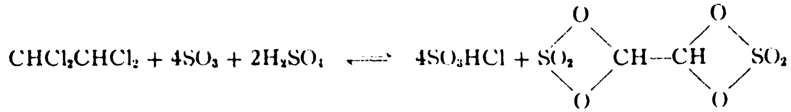
[126] A. E. Favorskii and V. O. Mokhnach, *Bull. Far Eastern Branch Acad. Sci. U.S.S.R.*, 1934, **9**, 3; *Brit. Chem. Abs.* **A**, 1936, 313; *Chem. Abs.*, 1935, **29**, 3981.

[127] M. Lesbre, *Compt. rend.*, 1935, **200**, 559; *Brit. Chem. Abs.* **A**, 1935, 611; *Chem. Abs.*, 1935, **29**, 3302.

[128] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**, 813.

[129] W. S. Calcott, A. E. Parmalee and J. L. Stecher, U. S. P. 1,983,535, Dec. 11, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 1086; *Chem. Abs.*, 1935, **29**, 817. British P. 453,271, 1936; *Chem. Abs.*, 1937, **31**, 1043; *J. Inst. Pet. Tech.*, 1936, **22**, 515A. *Cf.* British P. 450,152, 1936; *Brit. Chem. Abs.* **B**, 1936, 973; *Chem. Abs.*, 1936, **30**, 8245. *Cf.* S. Shappirio, U. S. P. 2,012,356, Aug. 27, 1935; *Chem. Abs.*, 1935, **29**, 6752. See also Chapter 30.

[130] V. Voorhees, U. S. P. 1,974,167, Sept. 18, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1934, **28**, 6997; *Brit. Chem. Abs.* **B**, 1935, 713.



Dichloroacetic acid may be secured from pentachloroethane and 97 per cent sulphuric acid at 130-170°C. The concentration of acid is maintained constant by adding water at intervals as needed.[132] According to Larson[133] acetic acid may be prepared by subjecting a mixture of 95 parts of carbon monoxide, 5 parts of ethyl chloride, and 25 parts of water to a temperature of 325°C. and a pressure of 700 atmospheres. A contact agent of active carbon or silica gel is advocated.

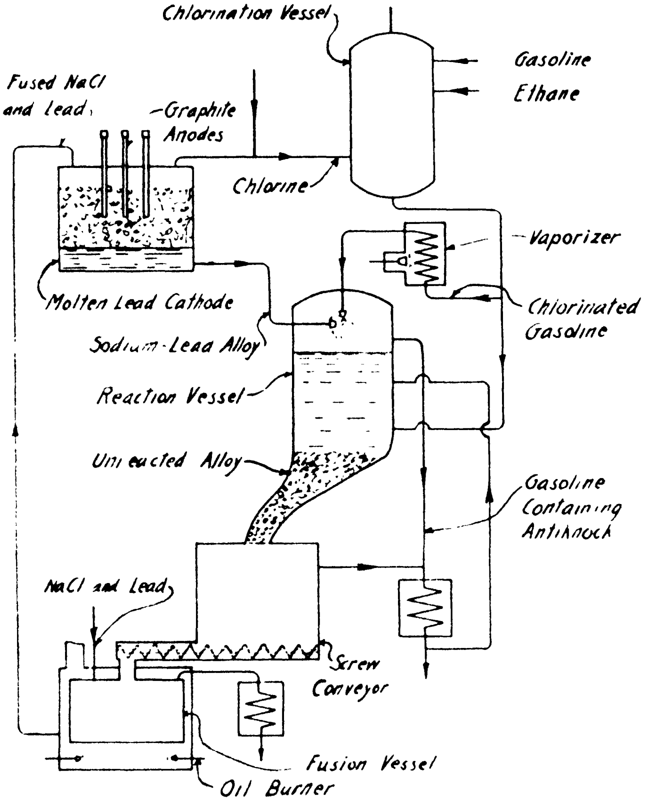


FIG. 194.—Manufacture of Lead Tetra-alkyls from Gasoline Hydrocarbons. (V. Voorhees)

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[131] M. A. Perkins, U. S. P. 1,999,995, April 30, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 4026. *Cf.* German P. 362,743, to Chem. Fabr. vorm. Weiler-ter Meer.; *J.S.C.I.*, 1923, **42**, 628A.

[132] British P. 424,047, 1935, to Compagnie de produits chimiques et electrometallurgiques Alais, Froges & Camargue; *Brit. Chem. Abs.* **B**, 1935, 396; *Chem. Abs.*, 1935, **29**, 4380. French P. 773,623, 1934, *Chem. Abs.*, 1935, **29**, 1437.

[133] A. T. Larson, U. S. P. 1,993,555, March 5, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1936, 264; *Chem. Abs.*, 1935, **29**, 2549. Canadian P. 353,452, 1935, to Canadian Industries Ltd.; *Chem. Abs.*, 1935, **29**, 8005.

Chapter 35

Extraction of Nitrogen Compounds from Petroleum

The presence of nitrogen compounds in shale oil[1] and coal oil[2] is well-known and the analytical constants and structures of many bases have been determined. These substances are composed, for the most part, of pyridines and their simpler substituted derivatives, such as pyridine carboxylic acid. On the other hand, investigations of petroleum fractions reveal that they contain a number of nitrogenous bodies whose structures are more complex.[3] These latter compounds seem to be hydroaromatic in character and therefore closely related to the alkaloids. Since naphthene hydrocarbons, containing rings of 5 carbon atoms, as well as polycyclic substances composed of aromatic or hydroaromatic nuclei, are found in petroleum and the acids derived from them known as naphthenic acids, those naphthenic compounds possessing nitrogen may be designated as naphthenic bases.

In general the nitrogen content of petroleum oils is low, in most instances being about 0.1 per cent. American petroleums appear to represent the two extremes, the paraffin-base oils from Pennsylvania containing only a trace and California oils the highest proportion. Peckham[4] reports that the latter has between 1.02 and 1.11 per cent of nitrogen. Caucasian oils, particularly those from the Baku fields,[5] are said to possess nitrogenous bodies to the extent of 0.006 per cent.[6]

McKee and Parker[7] have developed a method for the estimation of nitrogen bases (and unsaturated compounds) in petroleum distillates. They recommend extraction with 25 per cent acetic acid, which (they state) is more efficient than sulphuric acid which dissolves both nitrogen bases and olefins. Furthermore, acetic acid gives a clearer solution, dissolves more of the nitrogenous bodies and causes less polymerization than hydrochloric acid. To compare the three reagents, 5 cc. of oil were pipetted into a test bottle which had a neck of 6 cc. volume, graduated into 30 divisions. The bottle was cooled in iced water and 10 cc. (or 200 per cent by volume) of acid added. After stoppering, the bottle was allowed to remain in the cooling bath (with occasional shaking) for 30 minutes, except when acetic acid was employed. In the latter case 10 cc. of glacial acetic acid were added to the oil, the mixture shaken, then diluted with water and immediately centrifuged. More acid was then incorporated, to bring the oil layer within the range of the graduations and the container centrifuged for 2 or 3 minutes at about 1000 r.p.m. The percentage of extract was then ascertained from the decrease in volume of oil. Some of the results obtained in this manner are given in Table 172.

However, Bailey[8] reported that a completely satisfactory estimation of the

[1] See for example, I. B. Rapoport and Z. E. Kosolapov, *Khim. Tverdogo Topliva*, 1933, **4**, 323; *Chem. Abs.*, 1934, **28**, 6280. J. v. Braun, *Bull. soc. chim*., 1936, **3**, 1919.

[2] See, Ya. I. Khisin and V. K. Vasilchakova, *Goryuchie Slantzui*, 1934, **4** (2), 52; *Chem. Abs.*, 1934, **28**, 6988; *Brit. Chem. Abs.* **B**, 1935, 211.

[3] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[4] S. F. Peckham, *Amer. J. Sci.*, 1894, **48** (3), 250; *J.C.S.*, 1894, **66**, 456.

[5] E. Pyhala, *Petroleum Z.*, 1922, **18**, 1069; *J.S.C.I.*, 1922, **41**, 799A; *Chem. Abs.*, 1923, **17**, 372.

[6] P. J. Schestakow, *Chem.-Ztg.*, 1899, **23** (5), 41; *J.S.C.I.*, 1899, **18**, 260.

[7] R. H. McKee and H. H. Parker, *Ind. Eng. Chem.*, 1927, **19**, 1343; *Chem. Abs.*, 1928, **22**, 1032; *Brit. Chem. Abs.* **B**, 1928, 43.

[8] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

TABLE 172.—*Analysis of Test Solutions for Unsaturated Hydrocarbons and Nitrogen Bases.*

		Unsaturates and Nitrogen Bases.	
Stock	Reagent	Per cent Observed	Per cent Calculated
Mixture of Hexane, Amylene and Pyridine	Conc. H_2SO_4	22	25
	Conc. HCl	16	12
	29% HCl	18	12
	20% HCl	18	12
	10% HCl	22	12
Well Petroleum Gasoline	Conc. H_2SO_4	10-13	0
	25% Acetic acid	0	0
	Conc. HCl	2	0
	26% HCl	1	0
	4% HCl	2	0
20% Solution of Quinoline in Well Petroleum Gasoline	Conc. H_2SO_4	30	20
	25% Acetic acid	20	20
	Conc. HCl	20	20
	4% HCl	20	20
16% Solution of Quinoline in Well Petroleum Gasoline	Conc. H_2SO_4	24-25	16
	25% Acetic acid	16-20	16
Gasoline Solution of Quinoline after Washing with Sulphuric Acid	25% Acetic acid	0	0
Distillate Boiling up to 275°C. from Crude Shale Petroleum	Conc. HCl	10-11	—
	25% Acetic acid	13-14	—

naphthene bases in petroleum may be effected by employing a modified Kjeldahl method. Using this method the nitrogen content of California oil was found to be only 0.82 per cent as a maximum instead of the somewhat higher figures previously published.

EXTRACTION OF NITROGEN BASES

The extraction of these bases from petroleum fractions with sulphur dioxide, hydrochloric or sulphuric acid has received some attention. For example, Bailey[9] suggests treating the distillate at 20°F. with liquid sulphur dioxide to obtain a composite consisting of this substance, hydrocarbon oil and bases. An aqueous solution of the acid sulphites of the latter compounds is obtained on agitating the mixture with cold water. The free bases may then be secured by the addition of alkali, e.g., caustic soda, to the solution. This method is illustrated diagrammatically in Fig. 195. Another procedure involves passage of anhydrous sulphur dioxide into a body of oil.[10] Some of the resulting salts of naphthenic bases are precipitated and separated by filtration while others remain suspended in the oil. The latter may be extracted with water. Moser[11] advocates the use of sulphuric acid after preliminary treatment of the hydrocarbons with sulphur dioxide. Dilute acid (15 per cent) is employed in the first step to prevent formation of resins. After withdrawal of the aqueous acid from the oil, the latter is contacted with concentrated acid to effect removal of nitrogenous bodies.

Schestakow[12] reports that petroleum distillates may be subjected to the action of dilute sulphuric acid, the latter then neutralized and steam distilled. In this manner he secured (from a Caucasian petroleum distillate) 0.006 per cent of a brown liquid which had the characteristic odor of pyridine, was insoluble in water but readily soluble in alcohol. It distilled between 260° and 370°C. and on analysis was found to contain 6.60 per cent nitrogen, 85.72 per cent carbon and 8.09 per cent hydrogen. In some instances the oil may be filtered through fuller's earth before treating with acid. After neutralization of the latter the napthenic bases then liberated are extracted with ether. With a sample of Baku petroleum this method was said to lead to the segregation of mixed bases containing a high percentage of quinoline.[13] Hydrochloric acid is also suggested as a solvent in place of ether. The acid liquor is subsequently treated with salt and the bases salted out are dissolved in chloroform. Fractional distillation of the latter solution furnished pyridine and quinoline.[14]

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[9] J. R. Bailey, U. S. P. 2,035,583, Mar. 31, 1936, to Union Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 3627.

[10] D. L. Fox, U. S. P. 1,965,828, July 10, 1934, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1934, **28**, 5657; *Brit. Chem. Abs.* **B**, 1935, 345.

[11] F. R. Moser, German P. 496,224, 1928; *Chem. Abs.*, 1930, **24**, 3354. Canadian P. 302,849, 1930, to Simplex Refining Co., to Shell Development Co.; *Chem. Abs.*, 1930, **24**, 4623.

[12] P. J. Schestakow, *Chem.-Ztg.*, 1899, **23** (5), 41; *J.S.C.I.*, 1899, **18**, 260. *Cf.* G. H. Chlopin, *Chem.-Ztg. Rep.*, 1900, **24** (10), 88; *J.S.C.I.*, 1900, **19**, 429. *Ber.*, 1900, **33**, 2837; *Chem. Zentr.*, 1900, **2**, 1100; *J.C.S.*, 1901, **80** (1), 42.

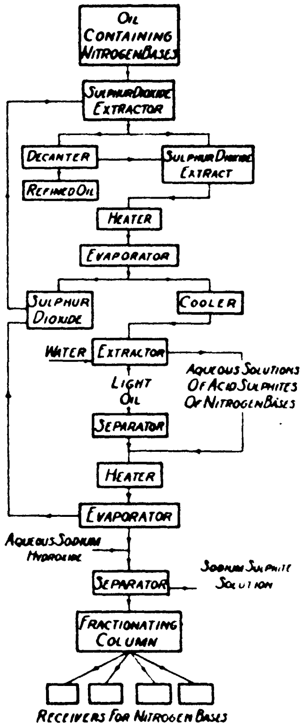

FIG. 195.
Flow Chart for Extraction of Nitrogen Bases from Petroleum Fractions. (J. R. Bailey)

STRUCTURE AND REACTIONS OF NAPHTHENE BASES

The structures of many of the nitrogen bodies contained in petroleum have not been ascertained possibly (as previously mentioned) because they break down during distillation and refining operations. However, the indications are these compounds are closely related to the alkaloids.

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[13] E. Pyhala, *Petroleum Z.*, 1922, **8**, 1069; *J.S.C.I.*, 1922, **41**, 799A; *Chem. Abs.*, 1923, **17**, 372. For a discussion of continuous refining processes employing sulphuric acid and fuller's earth, see S. E. Campbell, *Refiner*, 1935, **14**, 381; *Chem. Abs.*, 1935, **29**, 8302.

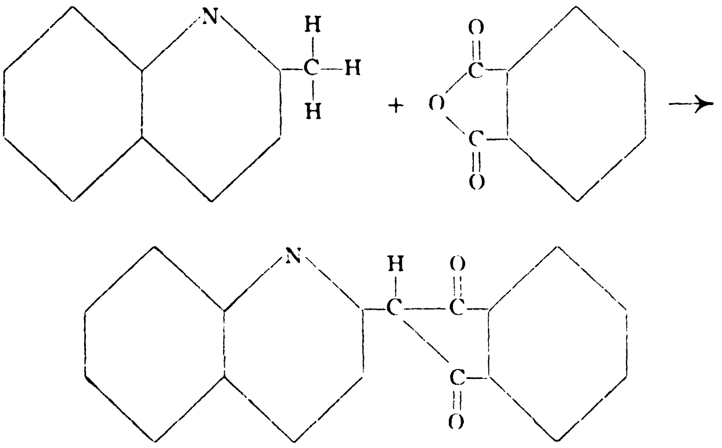
[14] J. R. Bailey, U. S. P. 2,035,584, Mar. 31, 1936, to Union Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 3629.

Distillation in vacuo of bases extracted from California petroleum resulted in the isolation of fractions whose molecular weights, analyses and boiling points are given in Table 173.[15]

TABLE 173.—*Naphthenic Bases from California Petroleum.*

Boiling Point °C.	Formula	Boiling Point °C.	Formula
139-140	$C_{12}H_{17}N$	223-225	$C_{15}H_{19}N$
197-199	$C_{13}H_{18}N$	243-245	$C_{16}H_{19}N$
215-217	$C_{14}H_{19}N$	270-275	$C_{17}H_{21}N$

These compounds reacted with platinum chloride to give crystalline precipitates and with chromic acid or neutral permanganate to form acetic acid, thus indicating the presence of short side chains and a tetrahydroquinoline ring.[16] Also these nitrogen-containing bodies united with bromine or iodine to yield addition products and with phthalic anhydride to furnish phthalones. The latter reaction suggested that the side chains were in the α- or γ-position in the nitrogen ring.



The first of the nitrogen compounds to be identified was 2,3,8-trimethylquinoline, which is present in a petroleum fraction boiling between 276° and 277°C. From this same portion an isomeric compound, $C_{12}H_{13}N$, and a base having the formula $C_{16}H_{25}N$ were also isolated. The separation of 2,3- and 2,4-dimethylquinoline from the cut boiling around 265°C. has been reported.[17]

The naphthene base $C_{16}H_{25}N$ represents a compound of the cyclopentane type, and may be the forerunner of structurally similar bases occurring in petroleum distillates. This substance is obtained from its picrate by heating the latter with ammonium hydroxide, washing with water and drying in a current of air. The material is a colorless, odorless, optically inactive oil, slightly soluble in water. It boils at 278.2°C. (746 mm pressure), has a specific gravity of 0.9391 at 20°C. (referred to water at 4°C.), and an index of refraction (with sodium light) of 1.5129 at 20°C. The structure originally assigned by Bailey and his co-workers was

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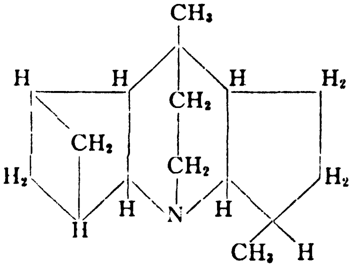
[15] C. F. Mabery and L. G. Wesson, *J.A.C.S.*, 1920, 42, 1014; *Chem. Abs.*, 1920, 14, 1831.

[16] For a discussion of these reactions, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[17] W. A. King and J. R. Bailey, *J.A.C.S.*, 1930, 52, 1245; *Chem. Abs.*, 1930, 24, 1864; ***Brit. Chem. Abs.*** A, 1930, 788.



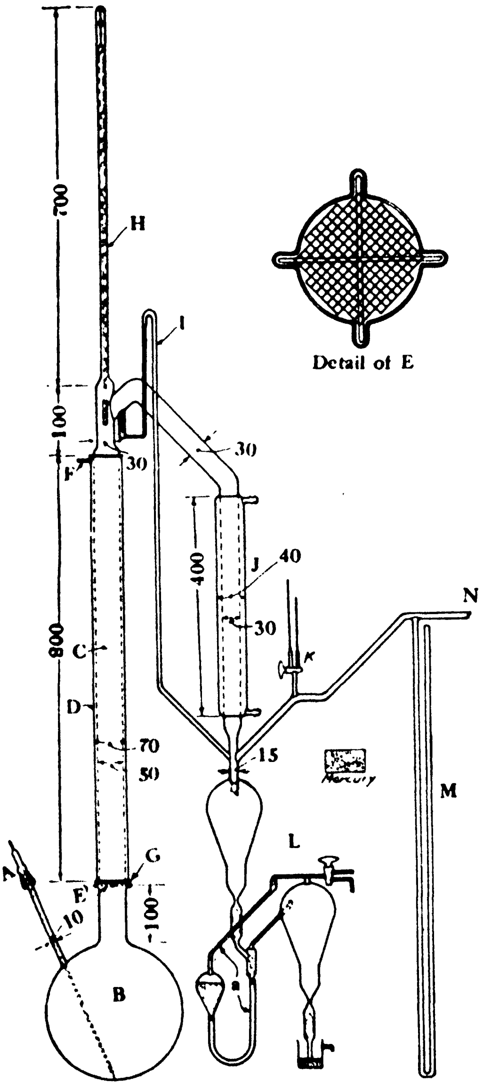


FIG. 196.
Vacuum Distillation Apparatus for Fractionation of Kerosene Bases. (E. J. Poth, W. A. Schulze, W. A. King, W. C. Thompson, W. M. Slagle, W. W. Floyd and J. R. Bailey)

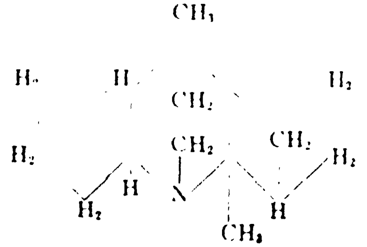
A.	Ground glass seal
B.	Five-liter glass
C.	Still column
D.	Column jacket
E.	Support for chain in column
F.	Air inlet to jacket
G.	Transite support for jacket
H.	Thermometer tube
I.	Capillary manometer
J.	Condenser
K.	Capillary leaks
L.	Receiver
M.	Manometer
N.	Lead to vacuum pump
a.	Rubber tubing

Courtesy Journal of American Chemical Society

According to Lackey and Bailey,[18] this saturated naphthenic base, like quinoline methylated in position 2, condenses with phthalic anhydride to form a phthalone. It appears that although formaldehyde does not combine with this base as readily as with quinaldine (2-methylquinoline) nevertheless the reaction does take place at 200°C. The product can be oxidized with nitric acid to yield a dibasic acid, $C_{14}H_{19}N(COOH)_2$. The latter compound, on heating furnishes a monocarboxylic acid, $C_{14}H_{20}NCOOH$, from which an oxygen-free base was secured. This latter step is effected by converting the acid into its sodium salt and distilling it in the presence of soda-lime. The distillate is taken up in dilute hydrochloric acid, the solution washed twice with ether, and the base, $C_{14}H_{21}N$, liberated by the addition of caustic soda.

These investigators (Lackey and Bailey) stated that the base containing 14 carbon atoms exhibited resistance to hydrogenation. From this characteristic it was concluded that the parent compound (possessing 16 carbon atoms) is completely saturated. An unsaturated molecule would have resulted had either of the two carboxylic groups in the dibasic acid come from cleavage of a methylene or ethylene bridge followed by oxidation of these groups. Therefore, the existence of at least two methyls in the base $C_{16}H_{25}N$ is said to be confirmed.

The latter compound acts in an analogous manner to that of 2,4-dimethylquinoline in its behavior towards formaldehyde and on oxidation of the resulting product to a dicarboxylic acid. The analogy is further extended in the easy elimination of one carboxyl group on heating. All these reactions are reported to suggest the same relative positions of the two methyls to nitrogen as exists in 2,4-dimethylquinoline, so the following revised formula (with methyls in the α- and γ-positions to nitrogen) has been proposed.[18a]



When bromine is added to this base a rather vigorous reaction takes place with evolution of considerable heat. A tough red gum is formed which slowly gives

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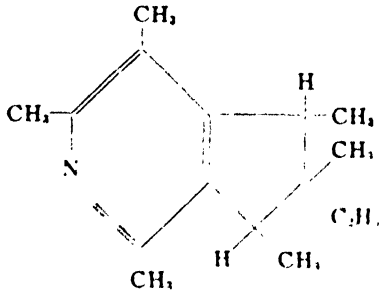
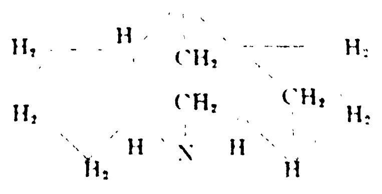
[18] R. W. Lackey and J. R. Bailey, *J.A.C.S.*, 1934, **56**, 2741; *Brit. Chem. Abs.* **A**, 1935, 357; *J. Inst. Pet. Tech.*, 1935, **21**, 50A; *Chem. Abs.*, 1935, **29**, 796.

[18a] J. R. Bailey (private communication) reports that some later work involving hydrogenation of the nitrogen base $C_{16}H_{25}N$ as well as its pyrolytic conversion to 2,3,6-trimethylpyridine appears to indicate it possesses a structure containing both a pyridine and an alkylated cyclopentane nucleus. One of several such possible structures may be represented by



off hydrogen bromide and is transformed into a heavy red liquid containing some free, admixed bromine. When agitated at 90°C. with 10 per cent caustic soda the liquid becomes colorless, and on drying and distilling under reduced pressure solidifies to a white crystalline solid with the following physical characteristics: m.p. 55.7°C., n_D^{60} 1.5268, n_D^{20} (subcooled liquid) 1.5431. This brominated base does not undergo the Fittig reaction,[19] is unaffected by heating with metallic sodium at 250°C., cannot be transformed into a Grignard reagent and is unchanged by prolonged refluxing with alcoholic or aqueous potassium hydroxide. Furthermore, it is not oxidized by either nitric acid or potassium permanganate in acetone solution. Efforts to replace the halogen by heating with silver acetate in glacial acetic acid were ineffective. The bromine derivative is unchanged on lengthy heating at 250°C. with sodium methylate as well as on treatment with moist silver oxide or alcoholic silver nitrate. Zinc and acetic acid, however, readily removed the halogen. Failure to brominate the base $C_{14}H_{21}N$, obtained by the elimination of two methyls from the compound $C_{16}H_{25}N$, indicates that bromination of the higher homologue replaces a hydrogen of a methyl group.

As previously mentioned, the lower homologue may be prepared by condensing the naphthene base $C_{16}H_{25}N$ with formaldehyde, oxidizing the product to a dibasic acid, heating to remove one carboxylic group and distilling the monobasic acid over soda-lime. For example, 1 volume of base and 35 volumes of formaldehyde (37 per cent) are heated at 190°C. for 8 hours in a sealed tube. At the end of this period a heavy oil separates. The latter may be dissolved in ether and extracted with dilute hydrochloric acid. Subsequent addition of caustic soda causes precipitation of a viscous, colorless syrup which apparently cannot be crystallized. Oxidation of the formaldehyde condensation product is accomplished by refluxing one volume of the substance with 40 volumes of 1:1 nitric acid for 4 hours. Evaporation of the resulting solution served to expel the nitric acid and the residue was a reddish solid, of indefinite crystalline form, insoluble in water, but soluble in alcohol, ether or acetone. The yield of acid was 47 per cent of the theoretical. Heat treatment of the latter substance at 235-240°C. under a pressure of 30 mm. brings about sublimation of a white crystalline product, a monocarboxylic acid ($C_{14}H_{20}NCOOH$) melting at 218-220°C. This is converted into its sodium salt, and distilled (under reduced pressure) at temperatures slightly higher than 360°C. from soda-lime. The distillate is washed with hydrochloric acid and ether and the base precipitated by addition of sodium hydroxide. The structure proposed for this compound is



EXTRACTION OF NAPHTHENIC BASES

A method for separating aromatic from non-aromatic bases has been developed by Perrins and Bailey.[20] This resolution depends upon the relative insolubility of aromatic base hydrochlorides in chloroform or ethylene dichloride. Both types of bases are dissolved in 1:1 hydrochloric acid and the solution extracted with the organic liquid. The latter, in turn, may be washed with water. The aqueous layer always contains a high concentration of aromatic base hydrochlorides. By employing this method 2,8-dimethyl- and 2,4,8-trimethylquinoline were isolated from a mixture of kerosene bases. The former compound was secured from a petroleum fraction boiling at 253° to 256°C. and the latter from the cut boiling at 273°C. Another method of separating the two types of bases is to dissolve the mixture in alcohol or acetone and add sulphuric acid, forming insoluble acid sulphates of the aromatic bases and soluble acid sulphates of the non-aromatic ones.[21]

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[19] Reaction of aromatic halide with alkyl halide in ether solution in the presence of metallic sodium.

[20] T. S. Perrins and J. R. Bailey, *J.A.C.S.*, 1933, 55, 4136; *Chem. Abs.*, 1933, 27, 5742; *Brit. Chem. Abs.* A, 1933, 1305. See also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

A process of microdistillation, termed amplified distillation, has been found of service in the separation of naphthene bases in distillates.[22] It was stated that some difficulty was experienced in working with small samples. This, however, was overcome by adding 15 to 20 volumes of an inert "carrier" solvent, whose function was to flush out the last traces of one cut before the next one began to distil. In the procedure, a fraction of bases is added to a petroleum oil boiling over a somewhat wider temperature range. After fractionation, the nitrogen-containing compounds are removed from admixed hydrocarbons by extraction with sulphuric acid, and precipitated in the form of picrates. In this manner the components of a complex mixture, even when the total volume is only a fraction of a cubic centimeter, are said to be segregated in the order of their boiling points. (See Table 174.) It was reported, in one instance, that from 130 cc. of a California pressure distillate there were secured seven pyridine homologues, quinoline and quinaldine.[23] In each instance the hydrochlorides of the naphthene bases were extracted with chloroform to withdraw non-aromatic derivatives. A very small quantity of nitrogen-containing compounds was recovered from the combined extracts, and this proved to be aromatic in character. It was concluded, therefore, that the occurrence of non-aromatic bases in cracked gasoline was not to be expected.

TABLE 174.—*Bases from California Pressure Distillate.*

Product	Boiling Point	n_D^{25}	Isolated as
2-Methylpyridine	129.3°C.	1.4983	Picrate
2,6-Dimethylpyridine	144°C.	1.4953	Picrate
4-Methylpyridine	145.3°C.	1.5029	Picrate
2,5-Dimethylpyridine	157°C.	1.4982	$HgCl_2$ salt
2,4-Dimethypyridine	158°C.	1.4984	Picrate
2,4,6-Trimethylpyridine	170.3°C.	1.4959	$HgCl_2$ salt
3,5-Dimethylpyridine	171.6°C.	1.5032	$HgCl_2$ salt
Quinoline	238.1°C.	1.6245	Picrate
Quinaldine (2-Methylquinoline)	247.6°C.	1.6093	Picrate

Sulphur dioxide is reported to be efficient for the partial separation of these nitrogeneous materials. Although it forms addition compounds with both aromatic and non-aromatic types nevertheless some of these are fairly stable while others dissociate rapidly at room temperature. For example, to resolve 2,4- and 2,3-dimethylquinoline, a kerosene fraction boiling between 263° and 267°C. is extracted with the liquid dioxide. The extracted portion is then treated with an alcoholic solution of picric acid. The resulting precipitate is leached with hot glacial acetic acid which dissolves all picrates except that of 2,4-dimethylquinoline.

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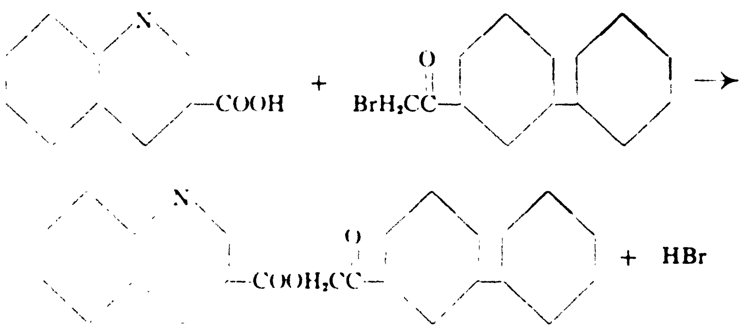
[21] J. R. Bailey, U. S. P. 2,067,704, Jan. 12, 1937, to Union Oil Co. of Calif.; *Chem. Abs.*, 1937, **31**, 1429.

[22] A. C. Bratton and J. R. Bailey, *Ind. Eng. Chem.*, 1936, **28**, 424; *Chem. Abs.*, 1936, **30**, 3681. J. R. Bailey, U. S. P. 2,085,287, June 29, 1937, to Union Oil Co. of Calif.

[23] A. C. Bratton and J. R. Bailey, *J.A.C.S.*, 1937, **59**, 175; *Chem. Abs.*, 1937, **31**, 1990.

These are orange colored needles. On cooling the acid the picrate of 2,3-dimethylquinoline crystallizes as microscopic hexagonal prisms melting at 231°C. Decomposition of the latter with alkali liberates the base as a white crystalline solid melting at 67°C. and boiling at 273°C.

Ganguli and Guha[24] point out that the nitrogeneous bodies extracted from an anthracene oil (boiling between 270° and 350°C.) cannot be separated by fractional distillation. That portion of the bases boiling from 180° to 200°C., under a pressure of 30 mm., was oxidized to carboxylic acids and their phenylphenacetyl esters prepared. To accomplish this the acids were dissolved in water, neutralized with caustic soda and a few drops of dilute hydrochloric (just sufficient to maintain a slight acidity) were added. Afterwards a solution of phenylphenacetyl bromide in ethanol was incorporated and the composite heated under reflux. On cooling, the esters precipitated.[25] Three phenylphenacetyl esters melting at 208°C., 201°C. and 101°C., respectively, were obtained. The first of these is reported to be that of quinoline (or isoquinoline) carboxylic acid and its formation may be represented as:



The fraction of bases boiling between 100° and 105°C. (under a pressure of 2 mm.) on reaction with an alcoholic solution of picric acid gave six picrates melting at 201°C., 181°C., 212°C., 230°C., 203°C., and 198°C., respectively. The structures of the first five were not determined, but the picrate melting at 198°C. was found to be a derivative of 5,8-dimethylquinoline. Of the others, the first four possessed the formula $C_{10}H_9N$ and seemed to be methyl quinolines or isoquinolines. The fifth one had the formula $C_{11}H_{11}N$ and was believed to be a dimethyl quinoline or isoquinoline.

Armendt and Bailey[26] investigated the fraction of kerosene bases distilling within the range of 215°-216°C. Fractional crystallization of the picrates, followed by distilling from soda-lime, yielded a colorless oil melting at 24.5°C. and boiling at 225.6°C. under a pressure of 750 mm. The formula of the base was reported to be $C_{13}H_{21}N$. On comparing with the naphthene base $C_{16}H_{25}N$ it was found that both resisted hydrogenation or dehydrogenation and were unaffected by alkaline permanganate. The basic compound ($C_{16}H_{25}N$) reacted with methyl iodide, but under similar conditions the methiodide of $C_{13}H_{21}N$ was not formed. The formula selected provisionally for the base containing 13 carbon atoms is

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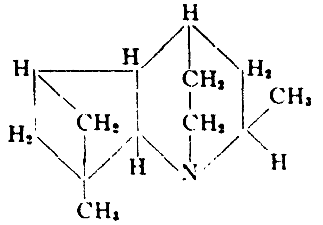
[24] S. K. Ganguli and P. C. Guha, *J. Indian Chem. Soc.*, 1934, 11, 197; *Chem. Abs.*, 1934, **28**, 4284; *Brit. Chem. Abs.* A, 1934, 782.

[25] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley & Sons, Inc., New York, 1935.

[26] B. S. Armendt and J. R. Bailey, *J.A.C.S.*, 1933, 55, 4145; *Chem. Abs.*, 1933, 27, 5743; *Brit. Chem. Abs.* A, 1933, 1305. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.



An interesting sidelight on the problem of the origin of nitrogen bases in petroleum has been noted.[27] To determine if non-aromatic bases (similar to those in petroleum) could be obtained from a stock containing proteins, carbohydrates and fats, an investigation was made of the compounds obtained on the distillation of cottonseed meal in a nitrogen-free lubricating oil.

The complexity of the cottonseed meal bases is reported to be comparable to those from petroleum. One of the marked dissimilarities is that one half of the first-mentioned substances are insoluble in petroleum ether. Another is that the higher boiling portions have a much greater nitrogen content than can be accounted for on the assumption of one nitrogen atom per molecule. Furthermore no evidence for the presence of a naphthene structure was obtained. The lower-boiling fractions (of cottonseed meal bases), however, did yield pyridine and a number of its homologues, identical with the products from coal, shale or bones. Coal-tar bases, such as quinoline, isoquinoline and lepidine, as well as the kero base[28] 2,3,8-trimethylquinoline were also found. Vacuum distillation of the high boiling protein-derived bases in an atmosphere of nitrogen led to the formation of colorless distillates which, unlike corresponding petroleum bases, soon darkened and precipitated tar. In the boiling range of 135° to 172°C. a total of 14 fractions of petroleum ether-soluble bases were secured. These consisted chiefly of pyridines, together with some pyrazines and diazines. The fraction in the range 172° to 215°C. had an abnormally high content of nitrogen and the presence of pyridine and quinoline was therefore considered excluded.

It is pointed out that these results should not be accepted as proof that petroleum bases are not of animal or vegetable origin. Bailey and his collaborators believe the assumption that the complex nitrogen compounds in crude oil arise from protein material does not necessitate the conclusion that a high temperature was involved in their formation. It would seem more probable that they resulted from bacteriological decay at ordinary temperature. The nitrogen in California petroleum does not exist in preformed basic compounds beyond a negligible amount and therefore the bases encountered in distillates are products of pyrolysis.

Nitrogen compounds of the pyridine series have been isolated from a fraction of Japanese shale tar.[29] According to Oparina and Smirnov[30] the shale-tar cut boiling between 140° and 145°C. may be condensed with benzaldehyde in the presence of zinc chloride. The three substances are reacted for 18 hours, and at the end of that period the portion distilling up to 200°C. is separated. On cooling this distillate distyrylpyridine is said to precipitate.

Another procedure for the recovery of methyl pyridines is based on carefully controlled precipitation with picric acid.[31] Application of this method to the low-boiling fractions of nitrogen bases from Japanese shale tar led to the isolation of a series of pyridine derivatives rich in α- and γ-alkyl substituted compounds. The majority of these contained methyl groups, though from the fraction boiling at 200° to 202°C. a base called pyrindane was obtained.

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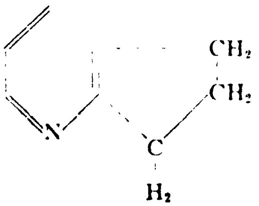
[27] J. Parker, C. L. Gutzeit, A. C. Bratton and J. R. Bailey, *J.A.C.S.*, 1936, **58**, 1097; *Chem. Abs.*, 1936, **30**, 5993; *Brit. Chem. Abs.* **B**, 1936, 1123.

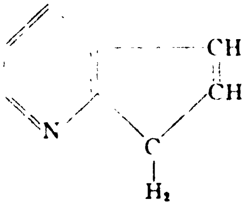
[28] Kero bases are the nitrogen-containing compounds obtained from the kerosene fraction of petroleum.

[29] T. Eguchi, *Bull. Chem. Soc. Japan*, 1927, **2**, 176; *Chem. Abs.*, 1927, **21**, 3197; *Brit. Chem. Abs.* **B**, 1927, 696. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[30] M. P. Oparina and B. Smirnov, *Khim. Farm. Prom.*, 1934, No. 4, 15; *Chem. Abs.*, 1935, **29**, 1820; *Brit. Chem. Abs.* **A**, 1935, 989.



However, the name pyrindine has been suggested for the compound



and on this basis pyrindane becomes 5,6-dihydropyrindine.

USES OF NAPHTHENIC BASES

One of the uses of petroleum bases is as a pickling inhibitor. Rings and Kettle[32] prepared a pickling acid from sludge resulting from the treatment of

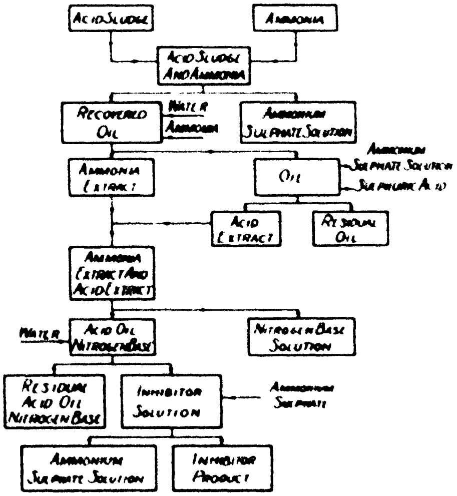


FIG. 197.
Flow Diagram for Manufacture of Pickling Inhibitor from Acid Sludge. (J. D. Rings and R. L. Kettle)

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[31] T. Eguchi, *Bull. Chem. Soc. Japan*, 1928, **3**, 227; *Brit. Chem. Abs.* **B**, 1929, 6; *Chem. Abs.*, 1929, **23**, 391

[32] J. D. Rings and R. L. Kettle, U. S. P. 2,042,412, May 26, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 4816.

kerosene with sulphuric acid. The sludge is first neutralized with ammonia and ammonium hydroxide, then added to the oily layer produced by the preceding step. (See Fig. 197.) In this manner a basic extract is secured and removed from the mixture. The basic and acid extracts may then be agitated together, causing the formation of a layer which contains a mixture of acid oil and nitrogen bases. The composite is hydrolyzed and admixed with ammonium sulphate to segregate the inhibitor.

Among the other applications proposed for naphthenic bases are as insecticides[33] and as inhibitors in the autoxidation of lubricating oils.[34] Investigation of nitrogen bases from a sulphur dioxide extract of transformer oil has indicated that they have germicidal properties comparable with that of phenol.[35] Soap-solution emulsions of these water-insoluble bases did not exhibit germicidal action on strains of *Eberthella typhi* and *Staphylococcus aureus*, but solutions in 0.1*N* hydrochloric acid did. Growth of these bacteria was completely inhibited with some of these bases in dilutions as high as 1:600. Control tests without the bases showed that the acid content of these solutions was not the active germicidal agent.

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[33] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[34] See Chapter 40.

[35] W. N. Axe, D. D. Henson and V. T. Schuhardt, *Ind. Eng. Chem.*, 1937, 29, 503.

Chapter 36

Oxidation of Petroleum Hydrocarbons. General Considerations

The great quantities of hydrocarbons available in crude petroleum or its fractions offer a source of materials for organic syntheses at relatively low cost. In consequence, the possibilities inherent in oxidation, which could convert these hydrocarbons into oxygen-containing substances of commercial value, make the study of such operations of industrial importance.[1] Such reactions offer a further advantage in that air is one of the raw materials. A great number of oxidation products have been reported as resulting from the various suggested processes, and in fact almost all possible permutations of oxy derivatives have been detected. For instance, alcohols, aldehyde-alcohols, aldehydes, ketones, aldehyde-acids, aldehyde-hydroxy acids, keto-acids, hydroxy-keto-acids and esters of these acids, both of the normal and of the lactonic ester type, have been found in the oxidized materials derived from a light petroleum distillate.[2] Oxidation carried to a very limited extent is effective as a dehydrogenation operation in converting paraffins to olefins, and naphthenes to aromatics. Certain processes have been suggested in which oxygen, after effecting such dehydrogenation, then serves as a catalytic agent for polymerization of the olefinic material to gasoline-like liquids.[3] The degree of accuracy required in the control of these oxidations varies both with the type of the initial hydrocarbon, and with the product desired. Ivanov and Savinova[4] reported a study of the oxidation of toluene, methylcyclohexane and *n*-heptane, using varying concentrations of hydrocarbon in air, and carrying out the reactions at different temperatures. In this instance hydrocarbons of differing degrees of complexity, acids, aldehydes, ketones and alcohols were obtained. It was found, however, that of these three seven-carbon hydrocarbons, *n*-heptane showed the greatest readiness to yield oxidation products before ignition occurred, the saturated cyclo-paraffin next, and the aromatic the least tendency to partial oxidation. Some hydrogen peroxide was found in the initial oxidation stage of the two non-aromatic hydrocarbons.

A great deal of work has been done in attempting to convert the higher hydrocarbons (e.g., paraffin wax) to acidic bodies which exhibit some properties analogous to those shown by the acids derived from natural fats and oils. Shoruigin and Kreshkov[5] investigated particularly the acids formed during oxidation (at 120°C.) of a wax melting at 52°C. The products consisted principally of hydroxy acids, lactones, lactides, fatty acids and their anhydrides, as well as unchanged and modified hydrocarbons, and lower partial oxidation products. The majority of these acids could not be distilled, even in a high vacuum. However, esterification with methyl alcohol yielded more volatile compounds. Distillation of the latter in vacuo permitted the separation of fractions which were mixtures of esters of hydroxy acids, and the average composition of which were represented by the empirical formulas

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[1] For further discussion of this subject, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[2] J. H. James, U. S. P. 2,009,661, July 30, 1935, to C. P. Byrnes; *Chem. Abs.*, 1935, **29**, 6358.

[3] See Chapter 26 for a discussion of polymer gasoline.

[4] K. I. Ivanov and V. K. Savinova, *J. Applied Chem.* (*U.S.S.R.*), 1935, **8**, 64; *J. Inst. Pet. Tech.*, 1936, **22**, 88A; *Chem. Abs.*, 1935, **29**, 6725.

[5] P. P. Shoruigin and A. P. Kreshkov, *J. Gen. Chem.* (*U.S.S.R.*), 1933, **3**, 825; *Chem. Abs.*, 1934, **28**, 6106; *Brit. Chem. Abs.* A, 1935, 196.

$$C_{13}H_{26}(OH)COOCH_3 \text{ to } C_{17}H_{34}(OH)COOCH_3$$

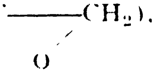
The more important industrial operations are, however, largely catalytic. Fokin[6] pointed out some years ago that the catalytic activity of a metal in oxidations or hydrogenations was proportional to its power to form different oxides or hydrides, respectively, and to the ease of the dissociation of these. Vanadium pentoxide, perhaps one of the most important oxidation contact agents in commercial practice, came into prominence during the 1920's, and has been used by many investigators with considerable success. If air and alcohol vapors are passed over the gently heated pentoxide (supported on asbestos) oxidation is vigorous enough to maintain the reaction temperature without external application of heat. In this instance the main products are acetaldehyde and acetic acid. According to Naumann, Moesse and Lindenbaum,[7] the catalytic activity of vanadium pentoxide is accounted for by the readiness with which the metal changes its valence from four to five and back, cyclicly, releasing active oxygen in each cycle, as follows:

$$V_2O_5 \rightleftharpoons V_2O_4 + O^*$$

Oxides of many of the heavy metals react similarly (e.g., the "blue oxides" of molybdenum), and have been proposed as applicable in a number of processes. On the other hand, metallic silver or copper, as well as their oxides, are useful particularly in the conversion of alcohols to aldehydes.[8] Oxidation of the type represented by the reaction of ethylene, carbon monoxide and steam to yield acids is catalyzed by a wide variety of substances, such as chlorides, metallic oxides, phosphoric acid and its acid salts.[9]

MECHANISM OF HYDROCARBON OXIDATION

The importance of hydrocarbon oxidation has inevitably lead to a great amount of study in an effort to understand and expound the mechanism of the reactions involved. Not only must slow oxidation of the hydrocarbons be comprehended for better control and production of intermediates, such as alcohols and aldehydes, but any wholly correct mechanism should include an understanding of the reactions taking place during explosive combustion. The latter is of special interest in consequence of its assistance to a more intelligent control of knocking in internal combustion engines. However, the very transient nature of the successive compounds formed during combustion renders a study of the problem exceedingly difficult. Much work has been done by spectroscopic means, making possible detection of radicals and compounds (particularly formaldehyde[10]) present in flames. However, the greatest amount of investigation directed toward complete elucidation of the mechanism has been done, probably, in connection with slow oxidation, since the records then are chemical analyses rather than spectrographic lines.

Three types of mechanism have been suggested. Bone proposed the hydroxylation mechanism by which oxidation of ethane, for instance, proceeds through the successive addition of atoms of oxygen at the carbon-hydrogen bond to produce first ethyl alcohol and then a dihydroxy ethanol which rearranges, with loss of water, to acetaldehyde.[10a] Steacie and Plewes advocate peroxidation whereby ethane (for example) is first dehydrogenated to ethylene, followed by addition of a molecule of oxygen to the unsaturated compound to give ethylene peroxide. This in turn reacts with ethylene to form ethylene oxide ( $\underset{O}{H_2C\text{———}CH_2}$), or with other intermediate oxy-compounds to furnish higher oxidation products. On the other hand, Norrish has developed a modification of the hydroxylation theory suggesting that there is a formation of free radicals which are the active chain-propagators.[11]

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[6] S. Fokin, *Z. angew. Chem.*, 1909, **22**, 1451; *Chem. Abs.*, 1909, **3**, 2646; *J.S.C.I.*, 1909, **28**, 893.

[7] A. Naumann, L. Moesse and E. Lindenbaum, *J. prakt. Chem.*, 1907, **75**, 146; *Chem. Abs.*, 1907, **1**, 1696; *J.S.C.I.*, 1907, **26**, 348.

[8] See Chapter 38.

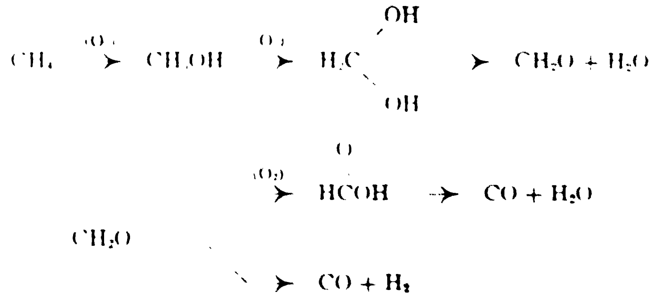
[9] See Chapter 39.

[10] L. Withrow and G. M. Rassweiler, *Ind. Eng. Chem.*, 1934, **26**, 1256; *Chem. Abs.*, 1935, **29**, 1235; *Brit. Chem. Abs.* **B**, 1935, 581. See also Chapter 44.

Most investigators agree on three necessary conditions which must be met: (a) that hydrocarbon oxidation proceeds only after the termination of an induction period which may endure for a fraction of a second or for several minutes; and (b) the mechanism must account for compounds known to be formed; and (c) there is a pronounced surface retardation phenomenon indicating that the reaction may be considered as a chain mechanism.[12]

Based on these concepts, three possible mechanisms have been developed. According to Norrish,[13] Bone has deduced his hydroxylation theory from the results of long continued experimentation and analytical work on the products formed. As a consequence, his explanation has been adapted to a static interpretation rather than to an understanding of the kinetics of the problem. Steacie and Plewes have paid particular attention to the kinetics of the problem, and the elucidation of the chain of reactions involved. Norrish's suggestion, involving a modification of the hydroxylation mechanism to include a reaction chain carried on by free radicals, has been put forward as adapting the rather static hypothesis. Bone favors the kinetics of chain reactions.

According to Bone and Gardner,[14] oxidation of methane proceeds as follows:



$$CH_4 \xrightarrow{(O)} CH_3OH \xrightarrow{(O)} H_2C\begin{smallmatrix}OH\\OH\end{smallmatrix} \rightarrow CH_2O + H_2O$$

$$CH_2O \xrightarrow{(O_2)} \overset{O}{HC}OH \rightarrow CO + H_2O$$

$$CH_2O \rightarrow CO + H_2$$

Norrish,[15] however, believes that this is not an adequate explanation, in that it does not account for the observed induction period, does not make provision for the action of catalysts and antiknock compounds and is inadequate to explain the effect of surface in reducing the observed induction period and also slowing the subsequent reaction. Finally, it leaves unexplained the observation that the ignition temperature of a given hydrocarbon-oxygen medium, under a given pressure, will vary when reaction tubes of different diameters are employed.

[10a] For the formation of methyl alcohol and ethyl alcohol during the oxidation of methane and ethane, respectively, see D. M. Newitt and J. B. Gardner, *Proc. Roy. Soc.*, 1936, **A154**, 329; *Brit. Chem. Abs.* **A**, 1936, 801; *Chem. Abs.*, 1936, **30**, 4460.

[11] See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, **1934**.

[12] However, Semenov (N. N. Semenov, *Acta Physicochim.* (*U.R.S.S.*), 1934, **1**, 113; *Chem. Abs.*, 1935, **29**, 6823) reports that the oxidation of ethane is not influenced by surface-volume ratio. He suggests further that the reaction is "doubly heterogeneous," in that chain branching and breaking both take place on the walls equally, thus, effectively cancelling the influence exerted by surface.

[13] R. G. W. Norrish, *Proc. Roy. Soc.*, 1935, **A150**, 36; *Chem. Abs.*, 1935, **29**, 4920; *Brit. Chem. Abs.* **A**, 1935, 1081.

[14] W. A. Bone and J. B. Gardner, *Proc. Roy. Soc.*, 1936, **A154**, 297; *Brit. Chem. Abs.* **A**, 1936, 801; *Chem. Abs.*, 1936, **30**, 4461. See also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, **1934**.

[15] R. G. W. Norrish, *loc. cit.*

Steacie and Plewes[16] report the hydroxylation mechanism is useful to predict products formed, but they do not consider it is satisfactory as a kinetic mechanism. Their observations show, furthermore, that the addition of excess oxygen may retard the rate of reaction after the induction period has passed, although the rate normally depends on some fairly high power of the concentration of the organic substance. This, they believe, taken in connection with the known retarding action of high surface-volume ratio, indicates that the reaction depends on a chain propagated by active molecules. Any excess oxygen tends to act as an "inert" diluent, and collisions between active hydrocarbon molecules and oxygen atoms tend to break the chain. The principal ending of the chain takes place at the surfaces of the vessel wall. However, since it has been observed that increased wall area decreases the induction period, though retarding the reaction once started, it is possible that the induction may involve a reaction between oxygen and, for instance, ethane absorbed on the surface of the reactor.

As previously mentioned, Steacie and Plewes are of the opinion that the first step in the oxidation of ethane is dehydrogenation to ethylene. In substantiation of this, they point to experiments in which ethylene-oxygen mixtures were heated until the induction period was passed and then ethane was added. This did not result in a new induction period, indicating that chains begun by ethylene may be continued by ethane. The complete oxidation of ethane, they believe, proceeds as follows:

$$\left.\begin{array}{lll} C_2H_6 + \frac{1}{2}O_2 & \longrightarrow & C_2H_4 + H_2O\ \text{(wall)} \\ C_2H_6 & \longrightarrow & C_2H_4 + H_2\ \text{(in the gas)} \end{array}\right\}\text{Induction period.}$$

$$\begin{array}{lll} C_2H_4 & \longrightarrow & C_2H_4^* \\ C_2H_4^* + O_2 & \longrightarrow & C_2H_4O_2 \\ C_2H_4O_2 + C_2H_4 & \longrightarrow & C_2H_4^* + \text{products} \\ C_2H_4O_2 + O_2 & \longrightarrow & \text{products} \\ C_2H_4O_2 + C_2H_6 & \longrightarrow & C_2H_4^* + C_2H_4 + H_2O_2 \\ C_2H_4^* + \text{surface} & \longrightarrow & C_2H_4\ \text{(Chain ends.)} \end{array}$$

(* Activated molecules).

One of the principal objections to this proposal mechanism is the fact that the hypothetical peroxide has not been detected by observers.[17] Steacie and Plewes[18] point out, however, that a substance suggested as the active agent in chain propagation should be unstable to secure continuity of the chain. However, according to Norrish[19] a further objection to this mechanism is that inert diluent gases do not exhibit the expected retarding action resulting from deactivation of active molecules:

$$C_2H_4^* + A \longrightarrow C_2H_4 + A$$

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[16] E. W. R. Steacie and A. C. Plewes, *Proc. Roy. Soc.*, 1934, **A146**, 583; *Chem. Abs.*, 1935, **29**, 985; *Brit. Chem. Abs.* **A**, 1934, 1331.

[17] Higher paraffins, however, do form detectable peroxides which are comparatively stable, when oxidized at the lower temperatures. Thus A. K. Plisov (*Bull. soc. chim.*, 1936, (5) **3**, 1274; *Chem. Abs.*, 1936, **30**, 7829) reports oxidizing a Grozny paraffin wax melting at 52°C. by passing oxygen at the rate of 200 liters per hour through the liquid wax at 140° to 160°C. Active peroxides were found in the products which liberated iodine from potassium iodide, and oxidized ferrous salts. These peroxides were said to be stable to heat. A second class of peroxides was reported which were described as inactive, and did not react to the ordinary tests for peroxides. Both classes of peroxides are decomposed, the investigator states, by reaction in the presence of acids or alkalies.

[18] E. W. R. Steacie and A. C. Plewes, *Can. Chem. Met.*, 1934, **18**, 217; *Chem. Abs.*, 1935, **29**, 26.

[19] R. G. W. Norrish, *loc. cit.*

where A represents an inert molecule incapable of taking part in the reaction, but serving to deactivate the activated molecules of the reactants by collision with them. This investigator has proposed a modification of the hydroxylation theory, which provides for the kinetics of chain reactions by the assumption that free radicals are produced. The existence and possibility of free radicals have been shown by many other workers, particularly in the field of high-temperature pyrolysis of hydrocarbons.[20] Norrish suggests, therefore, that the main series of reactions involved in the oxidation of methane is:

$$\begin{aligned} O + CH_4 &\longrightarrow CH_2^{*} + H_2O + 48\text{ Cal.} \\ CH_2^{*} + \tfrac{1}{2}O_2 &\longrightarrow H_2CO + 15\text{ Cal.} \end{aligned}$$

These are repeated indefinitely, since they are mutually self-sustaining. They are ended, however, in either of two ways, the first of which is a ternary collision:

$$O + CH_4 + X \longrightarrow CH_3OH + X^{*} + 88\text{ Cal.}$$

where X represents an inactive molecule which is activated by the collision. This reaction is the source of any methyl alcohol produced. Formaldehyde is, then, the primary product, and the alcohol will appear only as the result of such ternary collisions. Hence, it would appear in quantity only under high pressure, or when a high concentration of an inert diluent gas is present. The second type of reaction tending to terminate the chain is:

$$O^{*} + \text{surface} \longrightarrow \tfrac{1}{2}O_2$$

Norrish proposes that the induction period represents the slow reaction of methane and oxygen molecules to yield formaldehyde and water, on the surface of the vessel, with the result that increased surface speeds the induction. The formaldehyde so produced can be oxidized, at low temperatures, to the fairly stable performic acid, but at the temperatures prevailing in slow oxidation of the hydrocarbon, he believes that formic acid and an atom of oxygen result. Much of the atomic oxygen will remain adsorbed on the surface of the vessel, but a considerable proportion will pass into the gases, acting as starting points for the chains. Thus, the complete reaction chain for ethane becomes:

$$\begin{array}{lcl} \left.\begin{array}{lcl} C_2H_6 + O_2 & \longrightarrow & CH_3CHO + H_2O \\ CH_3CHO + O_2 & \longrightarrow & CH_3COOH + O^{*} \end{array}\right\} \text{Induction} \\ \begin{array}{lcl} O^{*} + C_2H_6 & \longrightarrow & CH_3CH^{*} + H_2O \\ CH_3CH^{*} + O_2 & \longrightarrow & CH_3CHO + O^{*} \end{array} \end{array}$$

This is ended by:

$$\begin{aligned} C_2H_6 + O^{*} + X &\longrightarrow C_2H_5OH + X \\ O^{*} + \text{surface} &\longrightarrow \tfrac{1}{2}O_2 \end{aligned}$$

Secondary reactions take place, breaking the ethane and its oxy derivatives to methane and methyl compounds:

$$\begin{aligned} CH_3CHO + O^{*} &\longrightarrow CH_3COOH \longrightarrow CH_4 + CO_2 \\ CH_4 + O_2 &\longrightarrow H_2CO + H_2O \end{aligned}$$

However, Norrish proposes a different series of reactions in the combustion of ethylene, as follows:

$$\begin{aligned} C_2H_4 + O_2 &\longrightarrow 2CH_2O + 60\text{ Cal.} \\ CH_2O + O_2 &\longrightarrow HCOOH + O^{*} \end{aligned}$$

which is ended by:

$$O^{*} + C_2H_4 + X \longrightarrow C_2H_4O + X.$$

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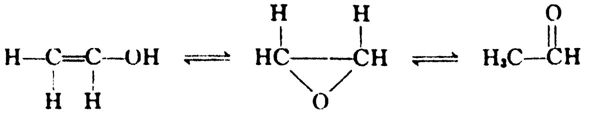
[20] **For a discussion of free radicals, see Chapter 2.**

Presumably, the compound C_2H_4O is vinyl alcohol, which is rapidly transformed into its isomers ethylene oxide and acetaldehyde:


vinyl alcohol ethylene oxide acetaldehyde

It will be noticed that following this mechanism, acetaldehyde will not be found as the primary product of ethane oxidation, but as an end product of the ternary collision in the ethylene oxidation. Norrish, however, reports that the aldehyde has been found in quantity among the products of ethane oxidation, but not in those from ethylene. Moreover, following this mechanism, methyl alcohol is unimportant in the oxidation of methane, and occurs only as an incidental product. According to Bone and Gardner,[21] methyl alcohol is a primary product, and they propose to modify the mechanism suggested by Norrish to the extent that methyl alcohol becomes the source of the active methylene radicals, thus:

$$\begin{array}{lcl} CH_3OH & \rightarrow & H_2C= + H_2O \\ H_2C= + O_2 & \rightarrow & H_2C=O + O^* \\ CH_4 + O^* & \rightarrow & CH_3OH \end{array}$$

Bone and Gardner point out that all stable intermediates postulated in this mechanism are found in quantity by analytical procedures.

Pease[22] studied the slow oxidation of propane, and from the results obtained, believes that the radical chain theory best accounts for the reaction. For this paraffin he proposes the following radicals:

$$\begin{array}{lcl} 2\,C_3H_8 & \rightleftharpoons & C_3H_8^* + C_3H_8 \\ O_2 + C_3H_8^* & \rightarrow & C_2H_6O + CH_3O^* \\ CH_3O^* + C_3H_8 & \rightarrow & CH_3OH + C_3H_7^* \\ C_3H_7^* + O_2 & \rightarrow & C_2H_4O + CH_3O^* \\ C_2H_4O + O_2 & \rightarrow & HCHO + CO + H_2O \\ 2\,CH_3O^* + M & \rightarrow & X \\ 2\,C_3H_7^* + M & \rightarrow & Y \\ CH_3O^* + C_3H_7 + M & \rightarrow & Z \end{array}$$

where M may be any molecule capable of combining with the radicals as indicated to yield the products X, Y or Z, making the radicals CH_3O- and C_3H_7- the active compounds in chain propagation.

Experiments on propane oxidation carried out by Pease and Munro[23] indicated that detectable amounts of a peroxide compound were formed during slow combustion. However, it was found that if the reaction tube was coated on the inside by a thin layer of potassium chloride, the peroxide was almost completely destroyed. Still, the reaction under these peroxide-free conditions was not appreciably slower than that in the clean (i.e., potassium chloride-free) tube.[24]

In conclusion, the work done with photochemical oxidations is of interest in understanding the mechanism of oxidation. Schumacher[25] reports, for instance, that the photochemical oxidation of rubrene indicates that the molecule may undergo fluorescence, stabilization, or direct addition of oxygen, after the absorption of light energy. A stable peroxide can be formed either by addition of oxygen to the stabilized rubrene molecule, or by deactivation of the activated peroxide. In any case, he states, the photochemical oxidation of rubrene represents direct absorption of light energy by the reactant, followed by a non-chain process. On the other hand, the chlorine-sensitized photo-oxidation of methane, methyl chloride and dichloromethane are chain reactions, involving the formation of short-lived peroxides. The first two reactions (i.e., the oxidation of methane and methyl chloride) are markedly inhibited by an excess of oxygen, whereas the oxidation of dichloromethane is not.

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[21] W. A. Bone and J. B. Gardner, *Proc. Roy. Soc.*, 1936, **A154, 297**; *Chem. Abs.*, 1936, **30**, 4461; *Brit. Chem. Abs.* **A**, 1936, 801.

[22] R. N. Pease, *J.A.C.S.*, 1935, **57**, 2296; *Chem. Abs.*, 1936, **30**, 1356; *Brit. Chem. Abs.* **A**, 1936, 33.

[23] R. N. Pease and W. P. Munro, *J.A.C.S.*, 1934, **56**, 2034; *Chem. Abs.*, 1934, **28**, 7244; *Brit. Chem. Abs.* **A**, 1934, 1329.

[24] See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[25] H. J. Schumacher, *Z. Electrochem.*, 1936, **42**, 522; *Chem. Abs.*, 1936, **30**, 7041.

EFFECT OF TEMPERATURE ON HYDROCARBON OXIDATION

In the reaction between the normal paraffins and oxygen, there is a fairly sharp spontaneous ignition temperature. Estradere[26] found this temperature of inflammation becomes progressively lower as the number of carbon atoms in the hydrocarbon molecule increases. Working with the normal paraffins from pentane through decane, and the higher homologues dodecane, tetradecane and hexadecane, this worker noted that the temperature of ignition for such hydrocarbons could be related by the expression $T = 192 + 756/n$, where T represents the temperature of ignition in degrees Centigrade, and n the number of carbon atoms in the hydrocarbon molecule. T was experimentally determined in the instances listed above by gradually raising the temperature of a mixture of the hydrocarbon with oxygen until a sudden, sharp rise indicated the ignition of the mixture.

Akita,[27] studying the similar problem of reaction temperatures, determined the "reaction starting temperature" by heating an oxygen-hydrocarbon mixture under constant volume conditions. The temperature at which a sudden abnormal increase in pressure occurred was taken as the point at which oxidation actively started. This investigator reported that for each normal hydrocarbon or alcohol, a series of reaction temperatures could be detected, the number of successive points being equal to the number of carbon atoms in the original molecule. Each succeeding abnormal pressure increase occurred at a temperature slightly higher than that of the preceding pressure rise, and at a temperature corresponding to the "reaction starting temperature" of the next lower normal hydrocarbon. An analogous series of reaction temperatures was detected for each of the normal aliphatic alcohols.

The same type of experimental procedure was applied to the study of the oxidation of aromatic hydrocarbons of the benzene and phenol series, but with these compounds no such series of reaction temperatures could be detected.

Gieb and Harteck[28] have reported a study of very low (liquid air) temperature oxidation reactions. These workers report that additive reactions, in which a stable compound can arise by the increase in valency of an atom of a second stable compound, occur with difficulty. However, addition occurs readily at low temperatures in the case of compounds having unsaturated bonds, or in which the subsidiary (and higher) valence is chemically active. Nevertheless, the union is apt to be so unstable as to form compounds unknown at room temperature. An additive product of ethylene and oxygen was found which decomposed at −110°C. to yield ethylene oxide, formaldehyde, acetaldehyde, carbon dioxide, and other liquid products. A similar treatment of acetylene resulted in carbon monoxide, ethylene glycol, formic acid, carbon dioxide, and water. Carbon monoxide adds oxygen only to a slight degree (1.3 per cent) to form carbon dioxide. Mono- and dimethylamine readily combine with atomic oxygen. At — 80° benzene gives a colorless, glassy material which decomposes into carbon monoxide and dioxide, formic acid and water.

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[26] S. Estradere, *Compt. rend.*, 1936, **202**, 217; *Chem. Abs.*, 1936, **30**, 2093; *Brit. Chem. Abs.* **A**, 1936, 432.

[27] Y. Akita, *J. Fuel. Soc., Japan*, 1934, **13**, 19; *Brit. Chem. Abs.* **B**, 1934, 487; *Chem. Abs.*, 1934, **28**, 4580.

[28] K. H. Gieb and P. Harteck, *Ber.*, 1933, **66**, 1815; *Brit. Chem. Abs.* **A**, 1934, 157; *Chem. Abs.*, 1934, **28**, 983.

OXIDIZING AGENTS OTHER THAN OXYGEN

Oxygen, particularly that in the atmosphere, has a great economic advantage over any other oxidizing agent, where it is applicable. However, various other oxidizing agents are of importance, especially the oxides of nitrogen. These latter compounds are reported to be useful in many instances as catalytic agents in processes employing air. According to Serbinov and Neiman,[29] the velocity of reaction between oxygen and ethane is increased several-fold by the addition of traces of nitrogen dioxide. Experiments were conducted with the reactants at a temperature somewhat below 500°C. and under 100 mm. pressure. It was found that the reaction velocity was higher, although the autocatalytic character of the normal oxygen-ethane oxidation was eliminated. These investigators did not believe that any direct interaction took place between the nitrogen compound and the hydrocarbon, but rather that the nitrogen oxide served to activate the oxygen present, according to the following series of reactions:

$$\begin{array}{lcll} NO_2^* + O_2 & \longrightarrow & NO_2 + O_2^* & \\ O_2^* + H_3C{-}CH_3 & \longrightarrow & C_2H_6O_2 & \\ O_2^* + O_2 & \longrightarrow & 2O_2 & \text{(chain ends.)} \end{array}$$

They suggest that a chain length of 100 may be possible in the complete reaction. James[30] described a method of oxidizing petroleum products using nitric acid, and the nitrogen oxides produced from it, as catalysts. In an example, he cites using a wax distillate which was atomized and injected into a reaction globe, maintained at 85° to 88°C. Simultaneously, nitric acid (1650 cc. of 70 per cent acid per 1100 cc. of wax distillate) was atomized and injected. The acid was recovered, to the extent of 85 per cent, in the liquids drawn off at the end of the reaction. The recovered oil containing oxidized substances (about 27 per cent of carboxylic acids) represented 95 per cent of the hydrocarbon injected. The operation was carried out at temperatures of 72° to 120°C. The investigator suggests that the mechanism involved the reduction of the nitrogen pentoxide, with oxidation of the hydrocarbon, and the subsequent regeneration of the higher nitrogen oxide by reaction with oxygen of the air. The oxide of nitrogen thus acts more in the rôle of carrier than catalyst.

Platonov and Shaikind,[31] however, investigated the oxidation of various hydrocarbons using nitric oxide as the oxidizing agent, rather than as a catalyst. In these experiments propane, hexane and heptane as well as gasoline (boiling from 63° to 77°C.) vapors were passed over catalysts in ratios from 1:1 to 1:3.5 with nitrogen monoxide. Various mixtures of aluminum, cerium and thorium oxides were used as catalysts (with and without carriers), also platinum black and vanadium pentoxide deposited on ceramic rings. When the milder catalysts (aluminum, cerium and thorium oxides) were employed, there were found some primary

[29] A. I. Serbinov and M. B. Neiman, *compt. rend. acad. sci. (U.S.S.R.)*, 1934, **2**, 297; *Brit. Chem. Abs.* **A**, 1934, 737; *Chem. Abs.*, 1934, **28**, 5321.

[30] J. H. James, U.S.P. 2,009,663, July 30, 1935, to C. P. Byrnes; *Brit. Chem. Abs.*, **B**, 1936, 683; *Chem. Abs.*, 1935, **29**, 6416. See also U. S. P. 2,009,662 and 2,009,664, July 30, 1935; *Chem. Abs.*, 1935, **29**, 6416; *Brit. Chem. Abs.* **B**, 1936, 683.

[31] M. S. Platonov and S. P. Shaikind, *J. Gen. Chem. (U.S.S.R.)*, 1934, **4**, 434; *Chem. Abs.*, 1935, **29**, 1769; *Brit. Chem. Abs.* **A**, 1934, 1329.

nitro compounds, sometimes primary amines, and considerable amounts of ammonium carbonate mixed with ammonium nitrate and nitrite in the products. A small proportion of the hydrocarbon was decomposed, forming unsaturated compounds and carbon dioxide. The ammonium carbonate is evidently the result of the union of ammonia (from the reduction of nitrogen monoxide) with water and carbon dioxide (from the oxidation of the hydrocarbons). The mechanism of the formation of the nitrates and nitrites was not clear, however, since air was excluded from the reaction zone. Employment of platinum and vanadium-pentoxide catalysts gave no organic nitrogen compounds, the chief products consisting of carbon monoxide, carbon dioxide, water, and free nitrogen, while most of the hydrocarbon remained unchanged. In none of the experimental runs was there any noticeable formation of organic acids, while nearly 30 per cent of the hydrocarbon was burned to carbon dioxide and water, with a considerable production of unsaturated compounds accounting for a major portion of the remainder. Addition of water vapor to the reactants increased thermal decomposition of the hydrocarbons without increase in the formation of organic acids. On the other hand, it has been reported[32] that the oxidation of hydrocarbon gas with nitrogen oxides may be controlled to yield hydrocyanic acid. High temperatures are needed, it is said, temperatures in the range of 1200° to 1400°C. being recommended. The mixed hydrocarbon and nitrogen oxides, together with a diluent such as nitrogen, carbon monoxide, or water is passed over platinum, platinum-rhodium or platinum-palladium catalyst at a temperature between 800° and 1400°C. but best between 1200° and 1400°C., as previously mentioned.

Steacie and McDonald[33] investigated the reactions involved when nitrous oxide (N_2O) was used as the oxidizing atmosphere in place of oxygen. Tests were made with methyl alcohol, ethylene, acetaldehyde, phosphine and carbon disulphide. Their results indicated uniformly higher ignition temperatures in the nitrous oxide atmosphere than in oxygen. With ethylene, the oxygen atmosphere reacts at a measureable rate at 300° to 450°C. On the other hand, nitrous oxide-ethylene mixtures interact only slowly at 530°C. With methyl alcohol, too, nitrous oxide reacts only at a much higher temperature (500° to 750°C.) than is required for the oxygen-methanol reaction. The temperatures required for acetaldehyde oxidation were even more widely separated. This aldehyde reacts with oxygen at 60° to 120°C., but with nitrous oxide a temperature of 450°C. was required. In the latter instance a very appreciable portion of the acetaldehyde disappearing was not oxidized, but thermally decomposed.

Various organic nitro compounds also serve as oxidants in certain reactions. Martin and Fletcher[34] report that aromatic nitro compounds such as the nitrobenzoic acids, nitrobromobenzenes and nitroanilines, for instance, will oxidize benzyl alcohol to benzoic acid, the yield varying with the temperature, alkalinity and nature of the nitro compound employed. The latter was, in no case, reduced to the primary amine. Either the azo, azoxy or hydrazo compound resulted. Zhukov[35] suggested using the salt-like bodies formed by aldehydes and ketones with nitric acid as oxidizing agents. Such bodies are obtained by dissolving the particular oxygenated compound chosen (e.g., camphor, menthone, cinnamic aldehyde) in strong nitric acid, slightly more than one molecular proportion of the acid being employed. The solution is cooled, and the crystalline precipitate separated. To effect oxidation, the organic compound to be treated is dissolved in the (molten) nitrate thus obtained, and the mixture allowed to react for some time at ordinary temperatures. The products are recovered by washing with water to separate the freed nitric acid.

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[32] British P. 446,277, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1936, 1150.

[33] E. W. R. Steacie and R. D. McDonald, *Can. J. Research*, 1935, **12**, 711; *Chem. Abs.*, 1935, **29**, 5727; *Brit. Chem. Abs.* A, 1935, 1213.

[34] E. L. Martin and W. A. Fletcher, *Trans. Kansas Acad. Sci.*, 1934, **37**, 135; *Chem. Abs.*, 1935, **29**, 2940.

[35] A. Zhukov, German P. 206,695, 1907; *Chem. Abs.*, 1909, **3**, 1803.

Hydrogen peroxide has been an important oxidizing agent, and may frequently be used in studying the constitution of an organic compound by oxidation. Giacomello and Mascarello[36] investigated the oxidation of the lower aliphatic acids in this way, and report that reaction takes place in several stages, with ultimate formation of carbon dioxide. The radicals liberated from the functional carbon atom which forms carbon dioxide, either form hydrocarbons or repeat the cycle with oxidation to alcohols, aldehydes and acids. Dupont and Dulou[37] report oxidizing cyclohexene in an ether solution of hydrogen peroxide, using osmic tetroxide as catalyst. In anhydrous ether, the reaction is very slow, the investigators state, and the products consist largely of acetaldehyde and acetic acid. The solvent is more readily oxidized than the cyclohexene. However, in methanol, ethanol, butanol or benzene solutions, cyclohexene is easily oxidized to cyclohexanediol.

The activity of ozone as an oxidizing agent is well known but, according to Briner and Carceller[38] it can act also as a catalyst in bringing about oxidation. Below 150°C. butane and pentane are oxidized to a very slight extent by oxygen, though in the presence of ozone appreciable proportions of aldehydes and acids are formed. At higher temperatures, ozone appears to function catalytically to bring about combination of the hydrocarbon with oxygen in the diatomic state. When ozone is not present, a certain amount of oxygen is found fixed in the recovered oxidation products. With ozone present (under conditions otherwise identical) the quantity of combined oxygen is greater than that represented by the ozone consumed plus the amount that would have been fixed had no ozone been present. This difference was taken to represent diatomic oxygen which had been brought into combination by the catalytic activity of the ozone.

Perhaps selenium dioxide is one of the most interesting of the other oxidizing agents used. It displays peculiar selectivity in its oxidation reactions, in some cases attacking unsaturated compounds at saturated carbon atoms once, and even two successive times, without affecting the double bond.[39] This dioxide is a relatively vigorous oxidizing agent, according to Astin, Moulds and Riley,[40] particularly at high temperatures, and it is therefore somewhat surprising that unstable, highly reactive compounds such as mesoxalic ester and ketohydrosuccinic ester can be prepared through its agency. Intermediate compounds may form an important part in the mechanism, and in support of this view unstable organoselenium compounds have been isolated. However, the investigators mentioned believe that the explanation is to be found in the reactions of the selenium atom itself, rather than in the oxide molecule. One peculiar manifestation of the oxidizing powers of this selenium oxide is displayed by flames being propagated in an atmosphere of selenium dioxide vapor. Ammonia, carbon disulphide, hydrogen sulphide and a large number of organic compounds burned in this way all give flames producing similar spectra which are characteristic of selenium and selenium dioxide, but not of the compounds undergoing oxidation. This phenomenon, it was believed, indicates that the selenium compound possesses the property of providing compounds undergoing combustion with oxygen atoms in a very low energy state. If the dioxide retains this property at lower temperatures (e.g., those temperature ranges in which it displays its specific oxidizing reactivity) then it is understandable that certain unstable compounds can be formed. As an example of this selectivity, Riley[41] reports that selenium dioxide will oxidize a methyl group adjacent to a carbonyl group. Thus, pyruvic aldehyde may be produced from acetone, or, hydrated phenyl glyoxal may be obtained from acetophenone:

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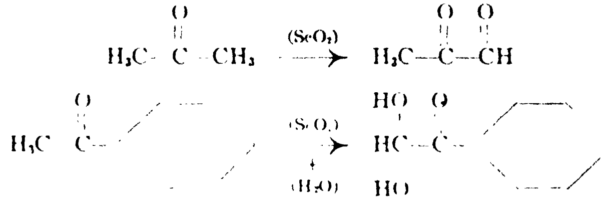
[36] G. Giacomello and G. Mascarello, *Gazz. chim. ital.*, 1934, **64**, 968; *Chem. Abs.*, 1935, **29**, 3303, *Brit Chem. Abs.* **A**, 1935, 472.

[37] G. Dupont and R. Dulou, *Compt. rend.*, 1936, **203**, 92; *Brit. Chem. Abs.* **A**, 1936, 1238; *Chem Abs.*, 1936, **30**, 8179.

[38] E. Briner and J. Carceller, *Helv. Chim. Acta*, 1935, **18**, 973; *J. Inst. Pet. Tech.*, 1936, **22**, 17A; *Chem. Abs.*, 1935, **29**, 6130. See also E. Briner, J. Carceller and I. Adler, Swiss P. 182,957, 1936; *Chem. Abs.*, 1936, **30**, 8240.

[39] A. Guillemonat, *Compt. rend.*, 1935, **200**, 1416; *Brit. Chem. Abs.* **A**, 1935, 852; *Chem. Abs.*, 1935, **29**, 5085. *Compt. rend.*, 1935, **201**, 904; *Brit. Chem. Abs.* **A**, 1936, 51; *Chem. Abs.*, 1936, **30**, 1357. See Chapter 39.

[40] S. Astin, L. de V. Moulds, and H. L. Riley, *J.C.S.*, **1935**, 901; *Chem. Abs.*, 1935, **29**, 6574; *Brit. Chem. Abs.* **B**, 1935, 1231. See also: S. Astin and H. L. Riley, *J.C.S.*, **1934**, 844; *Chem Abs.*, 1934, **28**, 5409; *Brit. Chem. Abs.* **A**, 1934, 869; S. Astin, A. C. C. Newmann and H. L. Riley *J.C.S.*, **1933**, 391; *Chem. Abs.*, 1933, **27**, 3193; *Brit. Chem. Abs.* **A**, 1933, 591; H. L. Riley and N. A. C. Friend, *J.C.S.*, **1932**, 2342; *Chem. Abs.*, 1932, **26**, 5903; *Brit. Chem. Abs.* **A**, 1932, 1108; H. L. Riley, J. F. Morley and N. A. C. Friend, *J.C.S.*, **1932**, 1875; *Chem. Abs.*, 1932, **26**, 4305; *Brit Chem. Abs.* **A**, 1932, 833.



Electrolytic oxidation of hydrocarbons has been difficult, and not generally attended by great success, since the hydrocarbons are not electrolytes, and must be emulsified with an electrolyte. However, a suggestion made by Hultman[42] offers an indirect electrolytic method which is said to overcome this difficulty. The investigator proposes that an apparatus be constructed holding sulphuric acid in a lower chamber, and hydrocarbon in the upper chamber. In the lower chamber a platinum anode (water cooled) is set under a glass cup, or funnel, which is carried on a tube running up through a division membrane to the upper chamber. A lead sheet surrounding the anode and inverted cup serves as cathode. On passing current between the electrolytic poles, the release of active oxygen at the anode serves to produce various highly oxidized sulphur acids, such as persulphuric acid, Caro's acid, as well as forming free oxygen, some ozone, and hydrogen peroxide. The release of the free gases causes a vigorous bubbling in the confined region under the glass cup, and the rising bubbles carry the highly oxidized acids with them, into the hydrocarbon chamber. A vigorous action is reported to take place here, giving the appearance of rapid boiling. The spent acid settles back through the hydrocarbon to a pipe which permits its return to the electrolyzing chamber below. (See Fig. 198.)

By means of the water-cooling coils, the temperature of the electrolyte is maintained near 23°C. According to Hultman, under these conditions vigorous oxidation results, but the low temperatures permit the stability and recovery of the products. Saturated compounds can be oxidized in this manner to acids, alcohols, aldehydes and ketones. Unsaturated hydrocarbons yield either similar compounds, or glycols and their oxidation products. For example, a petroleum ether (uncracked) consisting largely of pentane, hexane and heptane was oxidized by this method, and at the end of three to five minutes, the product contained butyl, amyl, hexyl and heptyl alcohols. After running for 10 to 15 minutes, the corresponding aldehydes were reported to be present in the electrolyte in considerable amount. After half an hour, fatty acids corresponding to these hydrocarbons were found in about 5 per cent concentration. When a cracked petroleum ether (boiling from about 40° to 70°C.) was used as the starting material, dihydric alcohols were produced. Continued oxidation yielded aldehydes and acids of a lower number of carbon atoms. A cracked gasoline furnished butyric and higher acids as well as higher glycols and their oxidation products. Hultman reports that catalysts, such as cerium sulphate, may be employed in addition to the electrolyte. It was further pointed out that the necessary factor in this method is that there be the shortest possible time interval between the production and utilization of the highly oxidized sulphuric acids. A mixture of sulphuric and persulphuric acids (made by reacting potassium persulphate and sulphuric acid) is practically ineffective.

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[41] H. L. Riley, U. S. P. 1,955,890, April 24, 1934, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1934, **28**, 4067.

[42] E. W. Hultman, U. S. P. 1,992,308, U. S. P. 1,992,309, and U. S. P. 1,992,310, Feb. 26, 1935, to Hultman and Powell Corp.; *Chem. Abs.*, 1935, **29**, 2732, *Brit. Chem. Abs.* **B**, 1936, 136.

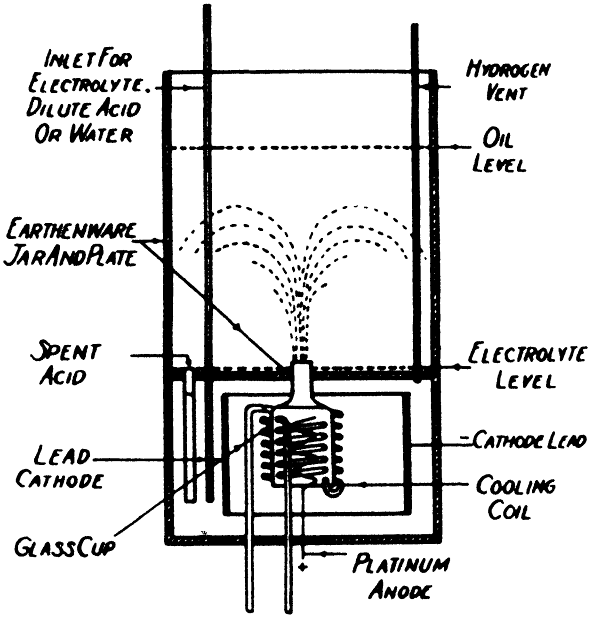

FIG. 198. Apparatus for Electrolytic Oxidation of Liquid Hydrocarbons. (E. W. Hultman)

PEROXIDES IN GASOLINES AND OILS

Although it has not been shown that the peroxides of the lower hydrocarbons can be isolated, the naphthenes and higher olefins do form comparatively stable peroxides. These latter compounds are generally powerful oxidizing agents, and serve to bring about the formation of gums and colored substances in gasoline and oils.[43] The naphthenes appear to be particularly prone to give peroxides, some of which are sufficiently stable to be concentrated to a considerable degree. Thus, Ivanov[44] reports oxidizing cyclohexane in the vapor phase at 316° to 370°C., in the presence of air, to an extent that yielded 6.5 grams of crude peroxide from 25.5 grams of cyclohexane. This required about ten hours. The crude product decomposed very rapidly on standing at room temperature, in the presence of light, to give about 52 per cent active oxygen. It could not be distilled (under 2 mm. pressure of nitrogen, at a maximum temperature of 170°C.) without decomposition. However, it was possible to remove volatile impurities, and water, by subjecting the crude product to 3 mm. pressure. The purified product was more stable, and released a greater proportion of active oxygen. By fractionation with diethyl ether, the material was separated into two substances. Analyses and molecular weight determinations indicated the empirical formula $C_7H_{14}O_7$ for the soluble fraction, and $C_7H_{14}O_6$ for the insoluble portion. These compounds were believed to be $(HOO)_2C_6H_9OOCH_2OH$ and $HOOC_6H_9(OH)OOCH_2OH$, respectively, from their reactions. It was thought that they resulted from the condensation of formaldehyde (formed during oxidation) with a peroxide of the formula $C_6H_9(OOH)_3$.

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[43] See Chapter 40.

[44] K. I. Ivanov, *J. Gen. Chem. (U.S.S.R.)*, 1936, 6, 470; *Chem. Abs.*, 1936, 30, 6344; *Brit. Chem. Abs.* A, 1936, 975.

Candea and Cristodulo[45] studied the oxidation of a light gasoline derived from a Rumanian Moreni crude oil, and compared the products obtained with those derived from the oxidation of pure cyclohexane, pinene, benzene, and mixtures of hydrocarbon fractions extracted from the original oil. Cyclohexane, and especially pinene, promoted the formation of peroxides at 320°C., while the aromatics were not only harder to oxidize, but retarded the development of peroxides. Oxidation of the pinene gave rise to gummy materials. The conclusion that naphthenes generally promoted peroxide formation (as did also pinene) while benzene and aromatics minimized this reaction appears to be confirmed by the work of Chernozhukov and Krein[46] with heavier hydrocarbon materials. These investigators worked with lubricating oils, and reported that an oil containing naphthenes and 15 to 20 per cent of aromatic hydrocarbons with paraffin side-chains formed no precipitate on oxidation, though the acid content increased due to oxidation of the side chains. In such material, the course of oxidation is the same as in the absence of naphthenes. However, if less than 10 per cent of aromatics is present, oxidation proceeds as in the case of purely naphthenic material. When an oil contained as much as 5 per cent of hydrogenated aromatic hydrocarbons, a precipitate formed on oxidation. The latter was found to consist largely of hydroxy acids, asphaltenes and carbenes. At higher concentrations of the hydrogenated aromatics, the insoluble bodies are almost entirely hydroxy acids. Aromatic tarry substances did not affect the oxidation, although naphthene-tars accelerated it.

It is believed by many investigators that the cause of autoxidation is to be found in the production of active peroxide substances. This autoxidation is a problem of considerable industrial importance, as it affects the storage of gasoline, the reactions of lubricating oils, the aging of rubber, gum deposition, and in many other ways affects the handling and usage of hydrocarbon materials. Autoxidation can be to a large extent controlled by the use of antioxidants, the choice of which being directed by the conditions under which it must serve. Dufraisse[47] has shown the antioxidant effect of an ether solution of hydroquinone on an unsaturated material such as sheet rubber. If one portion of a sheet of this material is dipped into the ether solution, and another portion is not, natural aging will harden the undipped portion, making it brittle and friable, while the dipped portion, protected by the antioxidant, remains pliable.[48] Lederer[49] has derived equations representing the rate of oxidation on either of two proposed mechanisms; that involving the absorption of an atom of oxygen, and that in which a molecule of oxygen is absorbed with the formation of a peroxide. The plot of time versus oxygen absorbed should, on purely theoretical grounds, be parabolic in the first case, and sigmoid in the second type of reaction. Experimental work indicated that reactions of the second type (peroxide formation) occur as the main ones with compounds containing two or more double bonds, and an active hydroxy or carboxy group, or a branched chain. Aromatic compounds with alkyl side chains possessing these characteristics react in a similar manner. In general, the reaction coefficient increases with increasing molecular weight, and the terpenes show the highest reaction rate of any hydrocarbons. A knowledge of oxidation characteristics is important in evaluation of transformer and lubricating oils, but determinations of the reaction velocities are cumbersome and unsatisfactory. It is usually sufficient to determine the "oxidation number," i.e., the amount of oxygen which one gram of oil will absorb in 100 minutes at 100°C., since in almost all cases the oxygen absorbed-time curve is nearly linear.

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[45] C. Candea and N. Cristodulo, *Bull. Sci. l'Ecole Polyt. Timisoara*, 1934, 5, 233; *J. Inst. Pet. Tech.*, 1935, 21, 125A; *Chem. Abs.*, 1935, **29**, 8304.

[46] N. I. Chernozhukov and S. E. Krein; *J. Applied Chem. (U.S.S.R.)*, 1935, **8**, 251; *Chem. Abs.*, 1935, **29**, 7057; *Brit. Chem. Abs.* **B**, 1935, 711.

[47] C. Dufraisse, *Bull. soc. encour. ind. natl.*, 1934, **133**, 107; *Chem. Abs.*, 1934, **28**, 3615.

[48] The general discussion of antioxidants, and the conditions covering their utilization and choice, will be found in Chapter 40.

[49] E. L. Lederer, *Petroleum Z.*, 1935, **31**, No. 44, 1; *Brit. Chem. Abs.* **B**, 1936, 10; *Chem. Abs.*, 1936, **30**, 2734.

Of the various types of mineral oils, the super-refined mineral white oils absorb most oxygen at 110°C., according to Muller.[50] Tests were made on various transformer oils at this temperature during periods up to 500 hours, though most of the tests were concluded at the end of 400 hours. It was found that the white oils absorbed by far the largest quantity of oxygen (400 to 10,000 cc. per 100 cc. of oil), the partially refined oils absorbed least, approximately 70 to 170 cc. per 100 cc. of oil, with the slightly refined oils intermediate, absorbing 100 to 250 cc. per 100 cc. The addition of a catalyst (copper stearate) increased the absorption in the latter two oils, but had little effect on the white oil. The products at the end of 400 hours consisted (in order of decreasing amount) of water, non-volatile saponified matter, ketones, fixed acidity, alcohols, and volatile acidity. Though peroxides formed in the early stages of the oxidation, at the end of the test period (when the oil was cooled) none was found.

THE TECHNICAL OXIDATION OF HYDROCARBONS

General Considerations. In technical processes for the partial oxidation of hydrocarbons, air or oxygen is most widely used as the source of oxygen, and natural or cracking gases frequently furnish the hydrocarbon material. Oxidation of the high molecular weight hydrocarbons of paraffin wax to carboxylic acids has attracted considerable attention. Perhaps because of the extreme difficulty of separating the complex compounds produced, petroleum hydrocarbons of the middle range (fuel oil and higher) have attracted somewhat less interest heretofore.

As Newitt and Townend[51] have pointed out, both natural and cracking gases contain upwards of 80 per cent of paraffin hydrocarbons, chiefly methane and ethane, with smaller proportions of olefins, higher paraffins, hydrogen, carbon dioxide and nitrogen. The enormous quantities of these gases available make them an attractive source of oxygenated compounds. That such operations can be economic is indicated by the work of these investigators on oxidizing ethane at 272°C. under 100 atmospheres pressure. Over 71 per cent of the carbon of the ethane consumed was found in the condensed products, which had the following composition:

[50] G. Muller, *Compt. rend.*, 1935, **200**, 1769; *Chem. Abs.*, 1935, **29**, 5255; *Brit. Chem. Abs.*, **B**, 1935, 709.

[51] D. M. Newitt and D. T. A. Townend, *World Petroleum Congr., London, Proc.*, 1933, **2**, 847; *Chem. Abs.*, 1934, **28**, 4871; *J. Inst. Pet. Tech.*, 1934, **20**, 252A.

Ethyl alcohol.....	51.0 Per Cent
Methyl alcohol....	28.0
Acetaldehyde.....	11.1
Acetic acid.......	9.0
Formaldehyde....	0.3
Formic acid.	0.6
	100.0

The principal considerations involved in technical partial oxidations of these hydrocarbons are the necessity for rigid heat control and the danger of explosive mixtures.[52] At room temperature and atmospheric pressure, mixtures of oxygen and methane containing between 6 and 58 per cent of the latter are explosive. At the higher temperatures employed in slow combustion these limits are further widened. The control of the temperature of the reaction must also take into consideration the great amounts of heat liberated according to the following equations:

$$2CH_4 + O_2 \longrightarrow 2CH_3OH + 2 \times 29{,}730 \text{ calories.}$$
$$2CH_3OH + O_2 \longrightarrow 2CH_2O + 2H_2O + 2 \times 20{,}640 \text{ calories.}$$
$$2CH_2O + O_2 \longrightarrow 2HCOOH + 2 \times 81{,}540 \text{ calories.}$$

Since the formation of methyl alcohol and formic acid (from methane and oxygen) results in a decrease in volume, and that of formaldehyde is accompanied by an increase in volume, increasing the pressure tends to displace the equilibrium in favor of the alcohol and the acid. High temperatures accelerate all three reactions and lead to complete oxidation to carbon dioxide and water. Hence, temperatures as low as possible, with high pressures, favor the development and stability of the alcohol. From the kinetic standpoint, high pressures would tend to accelerate the reactions, as would high temperatures. A certain degree of heat would be necessary to cause the reaction velocity to reach a practicable value, but the temperature must then be limited fairly closely. This effect may be obtained in a number of ways, but the use of high space velocities in the reaction chamber is, perhaps, one of the simplest.

Due to the close relationship between temperature and pressure in reactions of this type, the investigators could not entirely separate the effect of the two factors. Therefore, in studying the effects of pressure, a wide range was tested, employing in each case a temperature previously ascertained as the optimum for obtaining liquid products. The results so obtained (see Table 175) indicated the result of employing increased pressure.

TABLE 175.—*Effect of Pressure on Liquid Product Yield.*

Initial Pressure (Atmospheres)	Reaction Temperature °C.	Liquid Products in Per Cent of Carbon of Hydrocarbon Consumed	
		$81CH_4 + 10O_2$	$88.4C_2H_6 + 11.6O_2$
10	400	1.1	—
15	315	—	41.8
25	385	5.46	—
48	373	14.5	
50	294	—	39.1
75	279	—	46.0
100	270.5	—	50.4
149	341	19.6	

The experiments conducted in the circulatory system unit generally confirmed the results obtained statically. Thus, with the 10 per cent oxygen concentration in ethane, at 260 to 270°C., under 50 atmospheres pressure, the reaction took place slowly. A yield of a clear, water-soluble condensate containing 70 per cent of alcohols, and 20 per cent of aldehydes, with small quantities of acetic and formic acids resulted. By varying the rate of circulation, the ratio of methyl to ethyl alcohol could be varied between comparatively wide limits, although the total aldehydes and acids remained comparatively constant.

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[52] See Chapter 44.

Wiezevich and Frolich[53] reported an extended study of the partial oxidation of the saturated hydrocarbons of natural gas. It was found that methane (from natural gas) reacted with oxygen at temperatures near 500°C., though at higher temperatures, the tendency was toward the production of carbon oxides, rather than oxygenated derivatives. Of the products formed, methanol was present in preponderance, generally in quantities three to eight times the amount of formaldehyde. Some formic acid was produced as well as considerable amounts of water.

Since propane is liquid at normal temperatures at the high pressures employed, advantage was taken of the fact that oxygen is relatively soluble in the liquid propane. By saturating the liquid with air, an automatic control of the oxygen-hydrocarbon ratio below the explosive limit was maintained. Experiments indicated that the ideal conditions for the production of alcohols from propane were pressures above 130 atmospheres (up to 200 atmospheres, though higher pressures did not increase the formation of alcohols to a noteworthy extent), temperatures as low as practicable, time of reaction under 10 seconds, and oxygen concentration as high as the limits of explosiveness permitted. A representative reaction at 350°C. under 170 atmospheres pressure, in a steel tube, using 7.9 per cent oxygen concentration gave the results shown in Table 176.

TABLE 176.—*Oxidation Products of Propane.*

Product	Per Cent of Oxygen Converted to Compounds
Acetaldehyde (and formaldehyde)	9.4
Acetone	2.3
Methyl Alcohol }	
Ethyl Alcohol } approximate ratio of 13.4:8:5.2	26.6
Propyl Alcohol }	
Butyl alcohol	0.7
Acetic acid (containing formic)	4.1
Total Useful Products	43.1
Carbon Dioxide	10.1
Carbon Monoxide	9.7
Water	30.7
Unconverted oxygen	7.0

Variation of the propane-oxygen reaction with pressure was studied in a reactor immersed in a lead bath. A 6 per cent oxygen concentration and a long contact time were employed. The results showed that increase in pressure lowers the temperature at which appreciable reaction occurs. (See Table 177.)

TABLE 177.—*Variation of Propane-Oxygen Reaction Temperature with Pressure.*

Pressure Atmospheres	Reaction Temperature °C.
150	112.8
67	143.8
53	151.7

A circulatory flow system was developed for the production of acids from propane, the apparatus being so arranged that the acids were removed by neutralization, and the remaining products recirculated until they too were converted to acids. The propane-oxygen mixture was reacted at 400°C., then passed to a neutralizer and separator. The non-acidic products, and unreacted hydrocarbon, were returned for further reaction. The yields, in terms of liters per thousand liters of liquid propane, per pass were:

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[53] P. J. Wiezevich and P. K. Frolich, *Ind. Eng. Chem.*, 1934, **26**, 267; *Chem. Abs.*, 1934, **28**, 2249; *Brit. Chem. Abs.* **B**, 1934, 491.

Acetic acid	1.5
Formic acid	1.1
Intermediate products (remaining in system after run)	8.0
Formaldehyde	0.4
Propane lost as CO and CO_2	7.0
Water	9.5

Work with butane indicated that the reaction temperature varied with pressure in a manner similar to that of the propane-oxygen reaction. Further, the higher pressures used favored the production of higher, rather than lower, molecular weight alcohols and acids. As with propane, an acid-production run was made, recirculating the products for further oxidation to acids. In the case of butane, somewhat higher yields (3.62 liters per thousand liters of liquid butane per pass) of acetic acid were reported, and a lower (0.62) yield of formic acid. It was found, however, that increasing the isobutane content of the gas increased the formation of formic acid.

With pentane, oxidation under generally similar conditions gave somewhat better yields of higher alcohols, Wiezevich and Frolich reported. The products boiling from 80° to 110°C. consisted mainly of a mixture of ethyl and propyl alcohols. The higher alcohols were largely *sec*-amyl with small amounts of *ter*-amyl. The pentane consumption indicated a ratio of liters of pentane consumed to liters of product of 1.7:1. The run made with recycling of all products, except acids, changed the ratio of acids produced from 98 parts acetic to 2 of formic (found in the unrecycled product) to the following composition:

Acid	Per Cent by Volume
Formic	20
Acetic	53
Propionic	14
Higher	13

About 7 liters of acid were produced per 1000 liters of pentane per pass, while the loss to carbon dioxide and monoxide amounted to about 0.2 per cent of the pentane per pass.

Since the main products of the oxidation of pentane contained 2 or 3 carbon atoms per molecule, it was believed that the oxidation of heptane might lead to the production of 5 carbon compounds, such as amyl alcohols. The heptane used was a light gasoline fraction boiling between 70 and 97°C., containing all the heptane isomers present in casinghead gasoline. With this heavier hydrocarbon, longer contact times were needed. The operation was carried out at 225°C. under 135 atmospheres pressure (and hence presumably in the liquid phase). The products actually obtained were found to consist largely of alcohols in the heptyl-hexyl range, boiling between 140 and 180°C.

Klatt and Jellinek[54] have investigated the oxidation of kerosene, using a naphthene-base Russian oil, to produce the maximum of water-soluble compounds. No attempt was made to isolate the component hydrocarbons in this petroleum fraction. Manganese dioxide and vanadium pentoxide were tried as catalysts at temperatures ranging from 250 to 500°C. It was found that the manganese

[54] R. Klatt and H. Jellinek, *Petroleum Z.*, 1934, **30**, No. 12, 1; *Chem. Abs.*, 1934, **28**, 4883; *Brit. Chem. Abs.* **B**, 1934, 438. Also *Refiner*, 1936, **15**, 183; *J. Inst. Pet. Tech.*, 1936, **22**, 357A.

catalyst induced considerable pyrolysis. Vanadium pentoxide had a favorable effect on acid formation, improving with use. Reaction tubes of various types were tried, such as a copper tube packed with aluminum foil or turnings. In this case, acid-reacting substances were formed which were insoluble in water. It was concluded, however, that the most satisfactory arrangement of apparatus included a metal reaction tube, vanadium pentoxide catalyst, and diluent gases in the stream of reactants. Steam and nitrogen were used as diluents, and the amount and character of the yield were influenced to some extent by the proportion of diluents. The use of steam tended to inhibit secondary reactions, and very rapid cooling after passing the reaction zone aided in suppressing undesirable changes. The best method of vaporizing the kerosene was found to consist in dropping the oil on hot glass wool or pumice. Using 5 per cent vanadic oxide catalyst on pumice, at 440°C., about 7.5 per cent of converted material was obtained. The ratio of water to kerosene vaporized was 3 to 1. The reaction product so produced consisted of a water-soluble, yellow-brown material, highly acidic and pungent. A heavy white precipitate was formed at the oil-water interface consisting apparently of solid, carboxylic acids. It was impossible to characterize individual compounds in these products, but in certain cuts the presence of formic and acetic acids, formaldehyde, acetaldehyde and acetone was demonstrated.

In oxidizing the heavy hydrocarbons of paraffin wax, even lower temperatures are practicable. Burwell[55] reports that these heavy hydrocarbons may be oxidized in the liquid phase at temperatures in the range of 120 to 180°C., with or without a catalyst. With air, pressures of 200 to 500 pounds per square inch are employed; with oxygen, 150 to 250 pounds per square inch is sufficient. It was found that in the absence of catalysts, the straight-chain compounds were more readily attacked than other types. Under the mild temperature conditions indicated, the end (or methyl) group of the hydrocarbon is not attacked, but the reaction seems to involve primarily the second or third carbon of the chain, causing scission at the point of attack. (See also Chapter 43.)

Since oxidations are strongly exothermic reactions, in general, and are, as has been indicated, sensitive to temperature change, accurate control of the temperatures involved in the reactions is both necessary and difficult. In certain cases the cheapest of all heat-transfer media, water, is practicable, but in many instances the reactions must be carried out at temperatures above the critical for water.

Wiezevich and Frolich[56] used a number of different heat-transfer media while working on the oxidation of pentane, some for preheating the entering gas, and some for heat-transfer systems controlling the reactor temperature. Pentane was preheated to a temperature of 180°C. in a steel tube immersed in boiling naphthalene. The vapors were then passed into a steel reactor kept at about 240°C. by a boiling diphenyl oxide bath. At this point a small stream of pentane superheated to about 550°C. by a lead bath was injected, serving to start the reaction. Although the molten lead bath served as a heat reservoir for stabilizing temperature to some extent, it was somewhat handicapped where large quantities of heat were concerned at such a temperature as this (550°C.) because of its low specific heat. Transition temperatures (e.g., melting point, boiling point) were generally employed, since large quantities of heat may then be absorbed without change in temperature. Thus for cooling the reactor itself, where the highly exothermic reaction was taking place, the latent heat of vaporization of diphenyl oxide was employed as a controlling agent The latent heat of volatilization of various substances may be employed, or the latent heat of fusion of eutectics may be used.[57] Evidently the latent heat of vaporization is advantageous in that temperature may be controlled over some range by the application of pressure, while it may be accurately held at a chosen temperature by the large thermal capacity of the volatilization of the heat absorbing agent. Either elements such as mercury, or sulphur,[58] or compounds such as the aryl ethers, for instance diphenyl, naphthyl phenyl, or hydroquinone phenyl ether, may be used for this purpose.[59]

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[55] A. W. Burwell, *Ind. Eng. Chem.*, 1934, **26**, 204; *J. Inst. Pet. Tech.*, 1934, **20**, 158A; *Chem. Abs.*, 1934, **28**, 2169. See also Chapter 42.

[56] P. J. Wiezevich and P. K. Frolich, *loc. cit.*

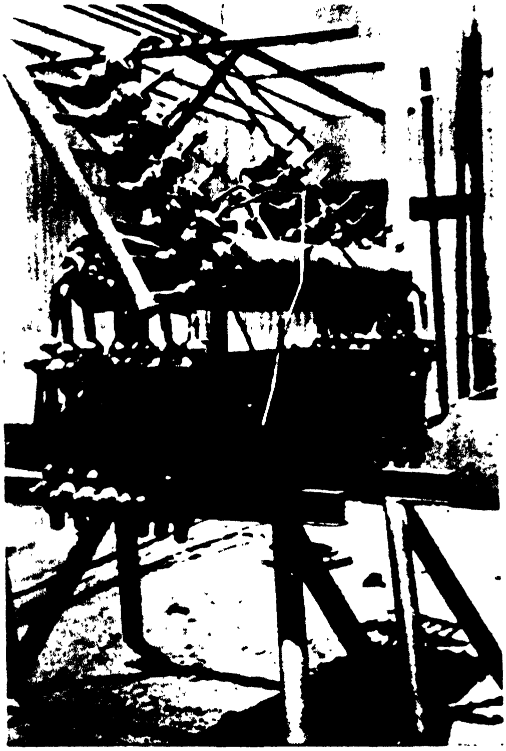

FIG. 199.
Reactor Employed for Hydrocarbon Oxidation at High Pressures. (P. J. Wiezevich and P. K. Frolich)

Courtesy Industrial and Engineering Chemistry

Egloff[60] suggests the rate of the reaction may be controlled chemically, by the addition of certain substances, such as tetraethyl lead. This method is applicable, for instance, in the oxidation of petroleum products (in the gasoline range) to alcohols, aldehydes and acids. Less than one per cent of the lead compound need be used, and the reaction may be carried out at 600°C.

Another problem is the separation of the complex mixtures of oxidation products. Those resulting from the treatment of hydrocarbons in the intermediate or fuel oil range of petroleum distillates become so complex that fractional distillation is frequently exceedingly difficult. It has been suggested that the reacted gases be conducted over a series of oil layers containing oxidation products and maintained at different temperatures. In this way, it is reported, fractional condensation of the various oxygen-containing compounds is obtained.[61] James[62] recommended a solvent process, using liquid sulphur dioxide to extract the more-highly oxidized bodies. The operation is carried out at a temperature of —18 or —20°C., and the products are separated by further cooling at —45°C. Sulphur dioxide may be recovered by evaporation.

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[57] A eutectic mixture having a melting point at the desired temperature may be chosen, such as the eutectic of sodium and potassium nitrates as in the oxidation of naphthalene to phthalic anhydride. (H. D. Gibbs, U. S. P. 1,599,228, Sept. 7, 1926, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1926, **20**, 3460; *Brit. Chem. Abs.* **B**, 1926, 1029.

[58] C. R. Downs, *J.S.C.I.*, 1926, **45**, 188T; *Brit. Chem. Abs.* **B**, 1926, 767; *Chem. Abs.*, 1926, **20**, 2990. U. S. P. 1,589,632, June 22, 1926; *Chem. Abs.*, 1926, **20**, 3015; *Brit. Chem. Abs.* **B**, 1926, 851.

[59] French P. 758,940, 1934, to Zahn & Co. G.m.b.H.; *Chem. Abs.*, 1934, **28**, 3150.

[60] G. Egloff, U. S. P. 1,939,255, Dec. 12, 1933, to Universal Oil Products Co.; *Chem. Abs.*, 1934, **28**, 1354; *Brit. Chem. Abs.* **B**, 1934, 872.

Oxidation in the Vapor Phase. In processes devised for obtaining oxidation products from hydrocarbons, both vapor- and liquid-phase methods have been mentioned, and it will be recalled that the progress of oxidation appears to differ in the two modes. It is evident that inasmuch as a large percentage of such operations are carried out at elevated temperatures, using hydrocarbons of low carbon atom number, these reactions may take place in the vapor phase. As pointed out previously, the oxides of metals of variable valence (such as vanadium pentoxide) are frequently employed as contact agents. However, methods involving catalysts such as the lower alkyl ethers have been suggested. Burke and Fryling[63] report that dimethyl or diethyl ether acts effectively in this capacity. In an example, liquid propane and diethyl ether were mixed (in proportions such as to yield 0.8 per cent ether in the vapors), and vaporized. The gases were then mixed with sufficient air to give 5.9 per cent oxygen in the resulting mixture. The gas mixture, under a pressure of 750 pounds per square inch, was passed through an aluminum-lined reaction tube 1/16 of an inch in inside diameter, and 20 inches in length. A flow of 15½ cubic feet of gas per hour was maintained through the tube, which was immersed in a bath of fused sodium and potassium nitrates kept at 350°C. (Contact time under these conditions was 0.185 second.) The products were immediately, and rapidly, chilled on leaving the reaction zone, and the liquid portion collected. The latter consisted of water, methanol, formaldehyde, acetaldehyde, together with higher alcohols, aldehydes, acids and ketones. This process is said to be quite sensitive to conditions of preheat. When the reactants were first heated to 357°C., the average molecular weight of the condensable products was 38.2. With a preheat of 370°C., the average molecular weight fell to 33.7. Using a lean natural gas (containing over 85 per cent methane), dimethyl ether as catalyst, and increasing the reaction temperature to 450°C., the products were methanol and formaldehyde. It was reported that yields approximately three times as great were obtained when employing the ether catalyst, as compared to those obtained without catalyst.

Burke[64] has proposed a method based on the fact that the temperature of reaction of a mixture of gaseous hydrocarbon and oxygen or air is lower in a tube of large diameter than in one of small diameter. In his process the reactants are heated to the proper temperature in a small diameter tube from which they emerge into a large chamber where reaction commences at once. He points out that in this manner it is possible to limit the zone of interaction to a relatively small volume and thus minimize changes in pressure and resultant fluctuations in the process. From the enlarged compartment the gases pass to small tubes, where efficient and rapid cooling is possible, bringing about a rapid extinction of the reaction. As an example, propane was vaporized and heated to 150°C., and the vapor mixed with air sufficient to give a 6.15 per cent oxygen concentration. Under a pressure of 750 pounds per square inch, the gases were passed through a 51 inch length of steel tube of 1/32 inch internal diameter. During this passage, the temperature was raised to 339°C. However, no reaction occurred under the conditions prevailing. The reactants were then conducted into a reaction zone having an internal diameter of 13/32 inch. and an internal length of 13/32 inch. The gases flowed at a rate of 15.4 cubic feet per hour, giving a reaction time of approximately 0.33 second, after which they again entered into a 1/32 inch steel tube, which extinguished the action. The products consisted largely of methanol, formaldehyde and other higher alcohols, aldehydes and acids.

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[61] J. H. James, U. S. P. 1,948,817, Feb. 27, 1934, to C. P. Byrnes; *Chem. Abs.*, 1934, **28**, 2889; *Brit. Chem. Abs.* **B**, 1935, 13.

[62] J. H. James, U. S. P. 1,970,535, Aug. 14, 1934, to C. P. Byrnes; *Brit. Chem. Abs.* **B**, 1935, 664; *Chem. Abs.*, 1934, **28**, 6156.

[63] S. P. Burke and C. F. Fryling, U. S. P. 2,018,994, Oct. 29, 1935, to Doherty Research Co.; *Brit. Chem. Abs.* **B**, 1936, 730; *Chem. Abs.*, 1936, **30**, 106.

[64] S. P. Burke, U. S. P. 1,978,621, Oct. 30, 1934, to Doherty Research Co.; *Chem. Abs.*, 1935, **29**, 176; *Brit. Chem. Abs.* **B**, 1935, 983.

Bludworth[65] reports that the oxidation of butane can be more accurately controlled by a method involving many recyclings of the reactants while a very small proportion of the ultimate oxidation to be obtained takes place at each pass. The latter condition is secured by using a very limited quantity of air at each pass. This investigator states that a maximum yield of methanol, acetone and acetaldehyde may be procured by this method. As an illustration, if an ultimate yield of eight gallons of liquid product is to be produced from 1000 cubic feet of butane, Bludworth recommends that not more than 0.0005 gallon be produced per cubic foot of butane per pass. He states that there should be not more than 1.25 per cent of oxygen in the reaction zone at any time, nor less than 0.4 per cent. By recycling the gases, fifteen or more times, introducing only a small fraction of the required oxygen in any one pass, interaction is controlled to prevent over-oxidation. Condensable liquids (methanol, acetone and acetaldehyde) are extracted from the gases after each passage through the reaction zone. In practice, about 96 per cent recycle and four per cent fresh butane (or propane) is used. The products then consist of about 8 gallons of methanol (75 per cent), acetone (12.5 per cent) and acetaldehyde (12.5 per cent).

Another method of controlled oxidation is to dilute the reactants with an inert gas, e.g., nitrogen. One procedure consists in cycling a quantity of inert gas in a closed ring system and introducing into this a hydrocarbon-air mixture, subsequently passing the commingled gases through a heated reaction zone and thence to a condenser to remove oxidation products by condensation.[65a] Excess inert gases are vented from the system and the remainder are returned to repeat the cycle. (See Fig. 200.)

Oxidation of gas oil in the vapor phase has been described by James.[66] In this case, vanadium, uranium or molybdenum oxides were used as catalysts. These were deposited on a screen of asbestos, through which the oil vapors, mixed with air, were passed. In one instance, a contact agent consisting of the "blue oxides" of molybdenum was used, coated on an asbestos screen one centimeter thick, and 4.4 centimeters in diameter. The gas oil was a fraction distilling around 275°C. Approximately 125 cc. of the liquid was volatilized and fed into the reaction zone each hour together with 1.6 times the quantity of air theoretically needed for the formation of aldehyde fatty acids. The catalyst was maintained at 270°C. during the run, and the rate of flow was such as to allow 0.32 second contact time. Tests of the exit gases showed 2.4 per cent of carbon dioxide and 1 per cent of oxygen escaping unchanged. At the end of one hour and 35 minutes, 150 cubic centimeters of liquid oxidation products had been recovered, consisting of about 85 per cent aldehyde fatty acids, and 15 per cent mixed aldehydes and unchanged hydrocarbons.

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[65] J. E. Bludworth, U. S. P. 1,923,610, Aug. 22, 1933, to Hanlon-Buchanan, Inc.; *Chem. Abs.*, 1933, **27**, 5341; *Brit. Chem. Abs.* **B**, 1934, 533.

[65a] J. E. Bludworth, O. R. Sweeney and F. C. Vilbrandt, U. S. P. 1,963,070, June 19, 1934, to Hanlon-Buchanan, Inc.; *Chem. Abs.*, 1934, **28**, 4743; *Brit. Chem. Abs.* **B**, 1935, 347.

[66] J. H. James, U. S. P. 2,010,086, Aug. 6, 1935, to C. P. Byrnes; *Brit. Chem. Abs.* **B**, 1936, 730; *Chem. Abs.*, 1935, **29**, 6414. See also J. H. James, U. S. P. 2,054,571, Sept. 15, 1936, to C. P. Byrnes; *Chem. Abs.*, 1936, **30**, 7581.

Ellis[67] pointed out that the antiknock value of a gasoline can be considerably increased by subjecting it to partial oxidation. The suggested process involves transfer of the hot hydrocarbon vapors (from a cracking operation) into a long flue-like reaction chamber into which air is admitted at a number of points. The fuel vapors taken directly from the cracking zone are still hot enough to react readily with oxygen, thus eliminating the need of preheating. Since oxidation is exothermic, Ellis recommends that the reaction chamber be cooled by heat exchange with raw oil passing to the cracking unit. In this manner the temperature can be maintained between 120° and 250°C. Pressures of 250 to 350 pounds per square inch are employed. The resultant product is found to be enriched in aromatic content, and contains various partial oxidation products having antiknock properties.[68]

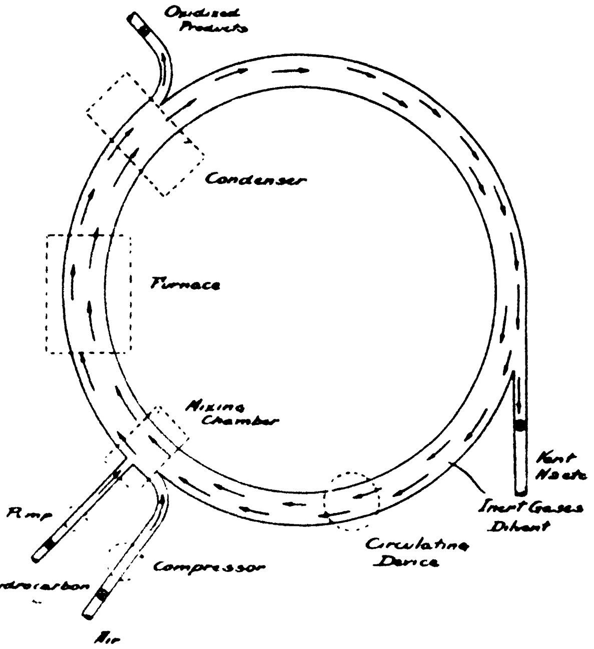

FIG. 200.—Schematic Diagram of Method for Partial Oxidation of Gaseous Hydrocarbons. (J. E. Bludworth, O. R. Sweeney and F. C. Vilbrandt)

Oxidation in the Liquid Phase. As previously mentioned, Wiezevich and Frolich[69] found that oxidation of pentane in the gaseous phase yielded largely propyl alcohol. This appeared to indicate degradation of the hydrocarbon molecule by the elimination of two carbon atoms. By analogy, it was thought that oxidation of heptane would yield amyl alcohols. Experiment showed, on the other hand, that the principal products were alcohols of the hexyl-heptyl range. It was suggested that the difference in behavior, under the conditions of oxidation, could be attributed to pentane reacting in the gas phase and heptane in the liquid phase. It appears then, that liquid-phase oxidations do not follow the course pursued by gas-phase operation. Further, certain other considerations must be taken into account in liquid-phase oxidation. Thus, for instance, it is frequently the practice to bubble the oxidizing gas (e.g., air) through the liquid hydrocarbon. If not all the oxygen is consumed, there may be an accumulation of the gas above the surface of the liquid, mixed with vapors from the hydrocarbon, which may lead to the formation of a dangerous explosive mixture. Penniman[70] suggests that this condition may be prevented by bubbling air through a depth (3 feet or more) of liquid hydrocarbon sufficient to completely deoxygenate it. This treatment is effected under superatmospheric pressure at 320° to 480°C. The liquid condensate obtained from this operation separates into two layers. The upper layer of oily material may be refined for use as an antiknock motor fuel, paint thinners, kerosenes, or similar products. The lower layer is an aqueous solution of organic compounds such as aldehydes, acids and alcohols. Penniman[71] proposed oxidation in the liquid phase at about 400°C., while the vapors produced are continuously withdrawn. Air is introduced into the liquid, and the volatile products formed are removed. From these the less volatile constituents are condensed and the resulting hot condensate is returned to the reaction vessel without further heating. The vapors are fractionated to yield motor fuel, alcohols, aldehydes, ketones and fatty acids.

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[67] Carleton Ellis, U. S. P. 1,976,696, Oct. 9, 1934, to Ellis-Foster Co.; *J. Inst. Pet. Tech.*, 1935, 21, 26A; *Chem. Abs.*, 1934, 28, 7483.

[68] Catalytic oxidation has been suggested as a means of freeing the exhaust gases of internal combustion engines of carbon monoxide and unburned hydrocarbon materials. J. Harger and A. Elliott (British P. 405,976, 1934; *Brit. Chem. Abs.* B, 1934, 439; *Chem. Abs.*, 1934, 28, 4869) propose conducting the exhaust through a Venturi injector, where air is admixed. The mixed gases then pass through a casing, over bauxite granules activated by impregnation with iron, copper, manganese or titanium compounds.

[69] P. J. Wiezevich and P. K. Frolich, *Ind. Eng. Chem.*, 1934, 26, 267; *Chem. Abs.*, 1934, 28, 2249; *Brit. Chem. Abs.* B, 1934, 491.

Heavier hydrocarbons such as paraffin wax are usually oxidized in the liquid phase at a lower temperature. Thus, Friedolsheim and Luther[72] pass liquid paraffin wax (at 100° to 220°C.) and air concurrently through two or more reaction chambers successively. These reactors are arranged one above another in such a way that a quantity of the hydrocarbon is maintained in each and reflux of the liquid is avoided while the gas bubbles through it. According to Nametkin and Zvoruikina[73] the oxidation of hydrocarbon waxes gives rise to lighter, volatile fractions, as well as the heavier acids. These lighter fractions were collected and after condensation were treated with sodium carbonate to remove acidic bodies, leaving a neutral or weakly acid oil containing the aldehyde-alcohol fraction. The latter was then washed with sodium carbonate and dilute sodium hydroxide, and afterwards with concentrated aqueous sodium acid sulphite. An oily liquid was separated from the resulting crystalline mass, and the crystals dissolved in water. The aqueous solution of the latter was extracted with ether, and the aldehydes recovered therefrom amounted to 7.7 per cent (123 grams from 1600 grams of crude aldehyde-alcohol fraction). Their boiling range indicated the presence of compounds containing five to nine carbon atoms. About 200 grams of the alcohols were recovered from the crude aldehyde-alcohol fraction. Distillation of the latter yielded cuts corresponding roughly to each of the normal alcohols from hexyl to dodecyl. These were further characterized by oxidation to the corresponding acids.

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[70] W. B. D. Penniman, U. S. P. 1,995,324, March 26, 1935; *Brit. Chem. Abs.* **B.** 1936, 438; *Chem. Abs.*, 1935, **29**, 2972.

[71] W. B. D. Penniman, U. S. P. 2,044,014, June 16, 1936; *Chem. Abs.*, 1936, **30**, 5403.

[72] A. v. Friedolsheim and M. Luther, U. S. P. 1,990,229, Feb. 5, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1832. See also French P. 779,895, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 5645.

[73] S. S. Nametkin and V. K. Zvoruikina, *J. Gen. Chem.* (*U.S.S.R.*), 1934, **4**, 906; *Chem. Abs.*, 1935, **29**, 2699; *Brit. Chem. Abs.* **B.** 1935, 132.

Chapter 37

Oxidation of Methane and Its Homologues

In this chapter the oxidation of gaseous and relatively low-boiling saturated aliphatic hydrocarbons is considered, not only for the preparation of alcohols, aldehydes and acids, but also from the standpoint of producing hydrogen, the oxides of carbon and unsaturated hydrocarbons. Such operations involve principally so-called quiet combustions and include as oxidizing agents, oxygen or air as well as other substances. The theories involving the mechanism of such reactions are discussed in the preceding chapter. Although several have been proposed to represent the various steps for methane and its homologues, no single explanation is without criticism.[1] Oxidation of the higher saturated hydrocarbons will be found in Chapters 42 and 43, as well as in a later section of this chapter.

OXIDATION OF METHANE

In the case of methane, as well as with its homologues, the oxidation may be made partial or complete, depending on the proportion of methane and oxygen and on the conditions of temperature and pressure, as well as catalytic materials present. For instance, Yoshikawa[2] oxidized methane under pressures of 1 to 100 atmospheres using catalysts of various degrees of effectiveness. Methanol and formaldehyde were formed as intermediate products but the amounts obtained varied in inverse proportion to the activity of the catalyst. When very reactive contact agents were employed these intermediates were absent from the final reaction mixtures. Burke and Fryling[3] treated methane with 10 per cent by volume of oxygen (50 per cent by volume of air) without the use of any catalytic material and obtained, as end products, acids and aldehydes. Reactions were carried out at 200-500°C. and under 200-1750 pounds per square inch pressure. On the other hand, when air and methane, containing only 15 per cent of the latter, were passed over a cobaltic oxide catalyst (Co_2O_3) at 500-550°C., transformation, almost completely to carbon dioxide and water, occurred. Use was made of this catalyst by Walker and Christensen,[4] in determining methane quantitatively in certain gas mixtures. They found further that nitrogen had no appreciable effect on the oxidation of methane under these conditions.

Newitt and Townend[5] conducted a series of experiments on the oxidation of methane with oxygen, in both static and dynamic systems, without the use of catalysts. In the former type, the apparatus consisted of a steel reaction cylinder of heavy construction fitted with inlet and outlet valves. In carrying out the experiments the reaction vessel was heated to the desired temperature and the hydrocarbon-oxygen mixture forced in until some predetermined pressure was attained. Temperatures were determined by means of thermocouples. The reaction could be stopped at any time merely by allowing the reactants to expand into a much larger vessel at room temperature. All products were analyzed so that a "balance" on the system could be determined. Some of the results obtained are shown in Table 178.

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[1] See also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[2] K. Yoshikawa, *Bull. Inst. Phys. Chem. Research* (Tokyo), 1931, 10, 413; *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), 25, 289; *Chem. Abs.*, 1935, 29, 2434

[3] S. P. Burke and C. F. Fryling, U. S. P. 1,991,344, Feb. 12, 1935, to Doherty Research Co.; *Brit. Chem. Abs.* B, 1936, 86; *Chem. Abs.*, 1935, 29, 2174.

[4] I. F. Walker and B. E. Christensen, *Ind. Eng. Chem. Anal. Ed.*, 1935, 7, 9; *Chem. Abs.*, 1935, 29, 1362; *Brit. Chem. Abs.* B, 1935, 261.

[5] D. M. Newitt and D. T. A. Townend, *Proc. World Petr. Congr.*, 1933, 2, 847; *Brit. Chem. Abs.* B, 1934, 823; *Chem. Abs.*, 1934, 28, 4871.

TABLE 178.—*Effect of Time on Reaction of Methane (8.1 vols.)—Oxygen (1 vol.) Mixture at 341°C. and 106.4 Atmospheres.*

Duration of Experiment	—Composition of Gaseous Medium Ml. at N.T.P.—						Oxygen Distribution	
Minutes	O_2	CH_3OH	HCHO	CO	CO_2	CH_4	CH_3OH:CO	+ CO_2
0	1000	—	—	10	—	8100	—	—
6.5	820	25.5	3.5	35	82	7890	1	7.8
7.25	600	50.0	7.0	52	142	7880	1	6.8
9.0	177	82.0	7.5	198	242	7540	1	5.7
12.0	Nil	142.0	4.5	300	198	7450	1	4.1
30.0	Nil	140.0	2.0	215	328	7410	1	6.2
1000.0	Nil	63.0	1.5	69	440	7520	1	15.2

As indicated by these results, prolonged contact of the heated gases results in decomposition of the intermediate products of oxidation. The investigators observed an induction period in the early stages, during which time little chemical change took place. It was shown also that by increasing the initial pressure of the system from 48.2 to 106.4 atmospheres, the temperature of an equivalent reactivity is lowered by 30°C. After a temperature of maximum yield is reached, the latter diminishes rapidly with further increase in temperature. This together with the fact that a relatively small temperature range (20°C. at the higher pressure) separates slow from rapid reaction rates, emphasizes the importance of accurate temperature control in oxidations of this type. Experiments carried out in a circulatory system, in general, confirmed results obtained by static operation.

Paris[6] also oxidized methane with oxygen under elevated pressure and concluded that the production of methanol in appreciable quantities depended upon the fact that as the pressure is increased, the following reaction increases at the expense of other possible conversions:

$$CH_4 + \frac{1}{2}O_2 \longrightarrow CH_3OH$$

The best yields of alcohol were obtained when the oxygen concentration was low and when the temperature did not exceed 450°C. On the other hand, methanol may also be prepared under milder conditions. Thus, Cristesco[7] conducted a 3:1 mixture of methane and air through boiling water (atmospheric pressure) containing, as catalyst, lead peroxide (PbO_2) mixed with granular copper oxide. A 57 per cent yield of methanol was obtained, along with some formaldehyde and methylal. The formation of methanol was explained as taking place according to the following equation:

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \longrightarrow CH_3OH + H_2$$

Extensive investigations have been carried on by Wiezevich and Frolich[8] on the direct oxidation of saturated hydrocarbons at high pressures. Laboratory and semi-commercial runs were made, both from the standpoint of producing intermediates such as alcohols and aldehydes, and also of obtaining acids as principal products. In dealing with methane, a natural gas rich in this material (2.1 per cent ethane, 6.3 per cent propane, 5 per cent nitrogen, remainder methane) was employed. In some instances, when concerned with the oxidation of mixtures of methane and ethane, this natural gas was enriched by incorporation of ethane. As oxidizing agent, 99 per cent oxygen was used, although similar results were obtained with air, provided the pressure was adjusted so as to compensate for the dilution by nitrogen. Reactions were carried on at various temperatures and the products removed by condensation and scrubbing. In Table 179 are summarized some of the results obtained using different catalysts:

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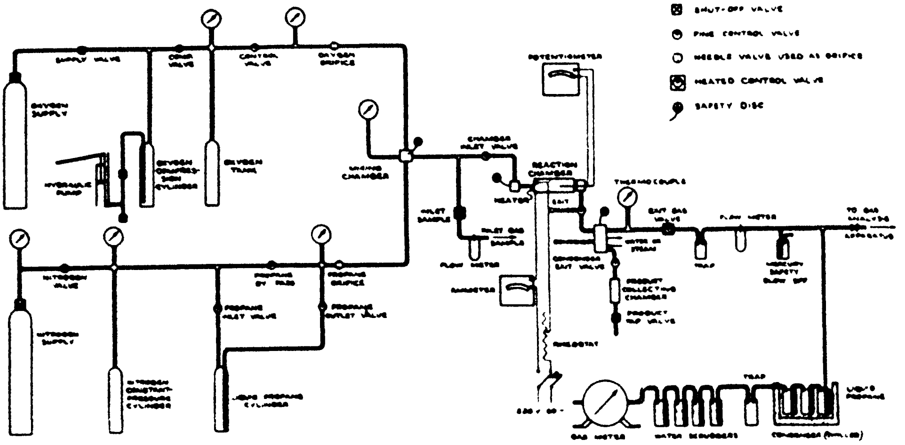
[6] A. Paris, *Chimie et industrie*, 1934, **31**, Spec. No., 411; *Brit. Chem. Abs.* **A**, 1934, 752; *Chem. Abs.*, 1934, **28**, 5806.

[7] J. Cristescu, *Fuel*, 1935, 14, 23; *J. Inst. Pet. Tech.*, 1935, **21**, 67A; *Chem. Abs.*, 1935, **29**, 4326.

[8] P. J. Wiezevich and P. K. Frolich, *Ind. Eng. Chem.* 1934, **26**, 267; *Chem. Abs.*, 1934, **28**, 2249; *Brit. Chem. Abs.* **B**, 1934, 491.



Courtesy Industrial and Engineering Chemistry

FIG. 201.—Sketch of Apparatus for High-pressure Oxidation of Hydrocarbons. (P. J. Wiezevich and P. K. Frolich)

TABLE 179.—*Oxidation of Methane and Ethane.*

CH_4 + Following % C_2H_6	Pressure Atm.	Exit Gas Liters/Hr.	Inlet O_2 %	Temp. °C.	Cat.	Liq. Products Wt. %	% O_2 to Useful Prod.
2	135	68	8.1	410	Iron	35 CH_3OH	15.2
2	132	70	8.6	410	Aluminum	28.7 CH_3OH 7.4 CH_2O 1.3 CH_2O_2	18
22	130	34.5	5.0	390	Nickel	30.0 CH_3OH 6.0 C_2H_5OH	14.4
22	131	58	6.0	392	Iron	32 CH_3OH 4 C_2H_5OH 1.5 higher alcs. 6.0 below 66°C.	

Bludworth[9] oxidized a saturated gaseous hydrocarbon by a stepwise procedure. The hydrocarbons and air were introduced into a reaction chamber, the entrance and exit temperatures of the gases being 200° and 230-480°C., respectively. Further injections of air were made at various points along the tube. The final reaction products contained, among other substances, methanol, acetone and acetaldehyde. Walker[10] has suggested a stepwise oxidation of natural gas in which a series of reaction chambers is employed. The gas is mixed with a small percentage of air, this amount being sufficient however to generate enough heat (by reaction) to maintain the desired conditions of temperature within the reaction chamber. The products then pass through a heat exchanger wherein the raw incoming gas is preheated, and the condensable oxidation products (alcohols and aldehydes) duly removed. The remaining, uncondensed gas is mixed with an additional portion of air and passed to a second reaction zone where again the heat of reaction maintains the desired temperature (425 to 500°C.) of the catalyst. As catalyst, this investigator found metallic platinum on pumice satisfactory. A further suggestion made, is that the oxidation may be carried only one step, thus getting a relatively small yield of alcohols and aldehydes, the exit gases being distributed as a commercial fuel gas. This is reported advantageous in that the exit gases contain no free oxygen, although natural gas does, in some instances, contain sufficient uncombined oxygen to render it highly corrosive to pipe lines and distributing equipment. On the other hand, if natural gas is treated with an insufficiency of oxygen at considerably higher temperatures (in the range of 1000°C.), acetylene is produced.[11] Among other catalysts which have been used in the partial oxidation of methane are included, the oxides of molybdenum,[12] copper, silver or zinc oxides in the presence of aluminum phosphate,[13] metallic silver and aluminum,[14] metallic platinum, palladium, chromium, iron or vanadium,[15] and the carbide-forming metals and their oxides.[16]

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[9] J. E. Bludworth, U. S. P. 1,923,610, Aug. 22, 1933; *Brit. Chem. Abs.* B, 1934, 533. C. L. Thompson, T. S. Bacon and J. E. Bludworth, U. S. P. 2,004,714, June 11, 1935; *Chem. Abs.*, 1935, **29**, 5123. Both assigned to Hanlon-Buchanan, Inc.

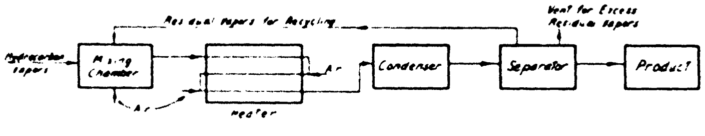

FIG. 201A.—Flow Diagram for Stepwise Oxidation of Gaseous Hydrocarbons.
(J. E. Bludworth)

Platinized silica gel[17] has been utilized in the complete oxidation of methane. Thus, a study of the effect of oxygen on mixtures of hydrogen and carbon monoxide with the gaseous saturated paraffins, using this catalyst, revealed that both hydrogen and carbon monoxide could be oxidized simultaneously at 300°C. in the presence of methane, but not when some of the higher members were present. Under these conditions methane was oxidized at about 375°C., ethane at about 250°C., propane at 150°C., and butane at 140-145°C., but the reactions were not complete even at 400°C.

If nickel catalysts and relatively high temperatures are employed, methane is converted into carbon monoxide and hydrogen, provided the correct proportion of oxygen is used. Padovani and Franchetti[18] employed temperatures of 850° to 950°C. At 900°C. less than 1 per cent of methane remained unchanged. The reaction is

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[10] J. C. Walker, U. S. P. 2,042,134, May 26, 1936, to Empire Oil and Refining Co.; *Chem. Abs.*, 1936, **30**, 4870.

[11] J. Burgin, U. S. P. 1,965,770, July 10, 1934, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 5474; *Brit. Chem. Abs.* **B**, 1935, 343.

[12] J. H. James, U. S. P. 2,036,215, April 7, 1936, to C. P. Byrnes; *Chem. Abs.*, 1936, **30**, 3627.

[13] J. C. Walker, U. S. P. 2,007,116, July 2, 1935, to Empire Oil and Refining Co.; *Brit. Chem. Abs.* **B**, 1936, 822; *Chem. Abs.*, 1935, **29**, 5456.

[14] P. J. Wiezevich and P. K. Frolich, *Ind. Eng. Chem.*, 1934, **26**, 267; *Brit. Chem. Abs.* **B**, 1934, 491; *Chem. Abs.*, 1934, **28**, 2249.

[15] J. C. Walker, U. S. P. 2,007,115, July 2, 1935, to Empire Oil and Refining Co.; *Brit. Chem. Abs.* **B**, 1936, 920; *Chem. Abs.*, 1935, **29**, 5456.

[16] W. K. Lewis and P. K. Frolich, U. S. P. 1,976,790, Oct. 16, 1934, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1935, 839; *Chem. Abs.*, 1934, **28**, 7263.

[17] K. A. Kobe and E. B. Brookbank, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 35; *Chem. Abs.*, 1934, **28**, 991; *Brit. Chem. Abs.* **A**, 1934, 269.

$$CH_4 + \tfrac{1}{2}O_2 \longrightarrow CO + 2H_2 + 8 \text{ kg. cal.}$$

At temperatures below 1000°C. sulphur in the reacting gases, in concentrations of 0.2 to 0.25 per cent, acts as a poison for the nickel catalyst.[19]

The internal combustion engine[20] has provided means for partially oxidizing hydrocarbons. Thus, a mixture of methane and air was introduced into an engine of this type, ignited, and the size of the combustion chamber then reduced and ignition discontinued. In this way it was possible to bring about the partial conversion (i.e., the formation of methanol and formaldehyde) by means of the adiabatic compression of the mixture and at the same time to retard combustion. This scheme has also been employed by Odell[21] who used the oxides of nitrogen as catalysts, aldehydes being among the products formed.

In addition to the action of oxygen or air on methane at elevated temperatures, the effect of other oxides has also been investigated. For instance, the influence of nitrogen peroxide (NO_2) on the ignition temperature of equimolecular portions of methane and oxygen has been investigated by Norrish and Wallace.[22] The ratio of methane to oxygen was held constant and the proportion of nitrogen peroxide varied. An induction period was noted which passed through a maximum with increasing partial pressure of the nitrogen oxide. A mechanism was proposed which involved the initiation of chains by oxygen which resulted from the oxide of nitrogen present. On the other hand, Krovatzkii[23] oxidized a gas rich in methane (52-56 per cent), using oxygen, and found that the oxides of nitrogen had no catalytic effect on the reaction. The maximum yield (32 per cent) of alcohols, without the use of catalysts, was obtained at 400-500°C. At higher temperatures decomposition of the oxidation products took place with the formation of carbon monoxide, carbon dioxide and water.

Methane reacts with carbon dioxide, at 300-500°C. and under elevated pressure, to give acetic acid.[24] Alkali or alkaline earth compounds having alkaline reactions, or phosphoric acid (H_3PO_4) or a phosphate having an acid reaction may be used as catalysts.

Steam acts on methane, in the presence of catalysts, at elevated temperatures and pressures, to give aldehydes and alcohols.[25] As an example, a mixture of steam and methane (1 to 5 volumes of steam to 1 volume of methane) was conducted, under a pressure of 180-250 atmospheres, over a catalyst mass (potassium bichromate and zinc oxide) heated to 350° to 450°C. The resulting oxygenated organic compounds consisted essentially of ethanol and the higher alcohols. Aldehydes, acids and ketones were practically absent. However, when oxygen was added to the original methane-steam mixture, and a zinc chromate-cobalt oxide catalyst used, aldehydes and acids were obtained as principal products, alcohols being almost completely absent. Further, the statement has been made that steam acts on carbon monoxide, in the presence of a catalyst such as chlorine or hydrogen chloride, to give formic acid.[26]

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[18] C. Padovani and P Franchetti, *Giorn. chim. ind. applicata*, 1933, **15**, 429; *Chem. Abs.*, 1934, **28**, 2853.

[19] V. A. Karzhavin and A. G. Leibush, *J. Chem. Ind. (Moscow)*, 1934, **10** (1), 34; *Brit. Chem. Abs.* **B**, 1934, 611; *Chem. Abs.*, 1934, **28**, 3189.

[20] Bellas Processing Corp., British P. 428,406, 1934; *Brit. Chem. Abs.* **B**, 1935, 661; *Chem. Abs.*, 1935, **29**, 6803.

[21] W. W. Odell, U. S. P. 1,939,018, Dec. 12, 1933; *Brit. Chem. Abs.* **B**, 1934, 872; *Chem. Abs.*, 1934, **28**, 1517.

[22] R. G. W. Norrish and J. Wallace, *Proc. Roy. Soc.* (London), 1934, **A145**, 307; *Brit. Chem. Abs.* **A**, 1934, 973; *Chem. Abs.*, 1935, **29**, 1700.

[23] Referred to by A. D. Petrov, *Coke and Chem. (U.S.S.R.)*, 1932, No. 9, 28; *Chem. Abs.*, 1934, **28**, 1983.

[24] H. Dreyfus, French P. 768,584, 1934; *Chem. Abs.*, 1935, **29**, 479.

[25] H. Dreyfus, U. S. P. 2,020,671, Nov. 12, 1935; *Chem. Abs.*, 1936, **30**, 484.

Metallic oxides alone have been employed to oxidize methane.[27] Arneil[28] passed methane-nitrogen mixtures at various temperatures through copper oxide (CuO) impregnated with other metallic oxides. Among the latter were the oxides of cerium, chromium, iron, molybdenum and uranium. Ferric oxide (Fe_2O_3) was found to be the most effective and reduced the temperature of complete oxidation by 200°C., when present in an amount representing 4 per cent by weight of the copper oxide. The conditions were adjusted so as to effect complete oxidation, which was determined by the amount of carbon dioxide present in the final gases.

On the other hand, under proper conditions hydrogen may result from the action of cupric oxide (CuO) on methane.[29] Sarmasel natural gas (98.6 per cent methane) was oxidized by this metallic oxide at temperatures ranging between 400° and 720°C. When oxidized at temperatures below 600°C., carbon dioxide was the only gaseous product formed. Above this temperature however, both carbon monoxide and hydrogen (up to 6.5 per cent) were formed. Carbon was deposited in all instances. In variance with this is the effect of stannic oxide (SnO_2) on this natural gas. At temperatures of 700-910°C. unsaturated hydrocarbons result, very little carbon and hydrogen being formed.

Zinc oxide also serves as an oxidant for methane. Thus, Candea and Kühn[30] subjected Sarmasel natural gas (containing 98.7 per cent methane) to zinc oxide at 850° to 950°C. By varying the velocity of the gas flow over the oxide, contained in a quartz tube (20 mm. diameter), two peaks of maximum oxidation were noted, one at a gas velocity of 6 liters per hour and the other at 10.5 liters per hour. These maxima were thought to be represented, respectively, by the reactions,

$$ZnO + C \longrightarrow Zn + CO \text{ and,}$$
$$ZnO + CH_4 \longrightarrow Zn + CO + 2H_2$$

The final gases contained principally carbon monoxide and hydrogen, in a ratio of 1:5.

The oxidation of ammonia-methane mixtures to hydrocyanic acid (HCN) has been investigated by Andrussow[31] who found that for good yields the ammonia, methane and oxygen (air) must be present in the proportions represented by the equation,

$$2NH_3 + 3O_2 + 2CH_4 \longrightarrow 2HCN + 6H_2O + 229{,}800 \text{ cal.}$$

At 1000°C., 58 to 63 per cent of the ammonia is converted into hydrocyanic acid, about 8 to 12 per cent to nitrogen, and 26 to 30 per cent remains unreacted. The process is distinctly catalytic, platinum serving the purpose satisfactorily but nickel being without effect.

OXIDATION OF ETHANE

Reaction between ethane and air or oxygen appears to proceed in a manner similar to that of methane.[32] Alcohols, aldehydes and acids result from partial, and carbon dioxide and water from complete, oxidation. Ethanol, an intermediate product, may be converted, under appropriate conditions, into acetaldehyde by further oxidation, by dehydrogenation, or by these two effects occurring simultaneously. Ethane, treated with oxygen under high pressure and at moderately high temperatures, without catalysts, yields ethanol along with other substances. Newitt and Townend[33] investigated this oxidation using 88.2 volumes of ethane to 11.8 of oxygen. The tests were carried on in a closed (static) system which consisted of an electrically heated steel chamber from which the reactants could be removed at any time and cooled rapidly to lower temperatures at which the reaction stopped. They found that the reaction of ethane with oxygen under these conditions is preceded by an induction period similar to that observed in the case of methane. Ethane-oxygen mixtures react, under these circumstances, at approximately 80°C. lower than methane-oxygen mixtures of identical proportions. The results obtained from experiments at various temperatures are given in Table 180.

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[26] J. C. Woodhouse, U. S. P. 2,001,659, May 14, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 4379; *Brit. Chem. Abs.* **B**, 1936, 919.

[27] For a further discussion, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**, 846.

[28] A. Arneil, *J.S.C.I.*, 1934, **53**, 89T; *Brit. Chem. Abs.* **A**, 1934, 608; *Chem. Abs.*, 1934, **28**, 3377.

[29] C. Candea and J. Kühn, *Petroleum Z.*, 1936, **32** (35), 11; *Brit. Chem. Abs.* **A**, 1936, 1212.

[30] C. Candea and J. Kühn, *Bul. soc. chim. Romania*, 1935, **16**, 121; *Chem. Abs.*, 1935, **29**, 4280; *Brit. Chem. Abs.* **A**, 1935, 592.

[31] L. Andrussow, *Angew. Chem.*, 1935, **48**, 593; *Chem. Abs.*, 1935, **29**, 8244; *Brit. Chem. Abs.* **A**, 1935, 1392.

[32] W. A. Bone and W. E. Stockings, *J.C.S.*, 1904, **85**, 693; *J.S.C.I.*, 1904, **23**, 601.

TABLE 180.—*Effect of Temperature on Reaction of Ethane-Oxygen Mixture (88.2:11.8 volume ratio) under 100 Atmospheres.*

Initial Temp. °C.	Duration of Reaction Mins.	Percentage of the Carbon of Ethane, Surviving as:						Total Liquid Products Per Cent
		C_2H_5OH	CH_3OH	CH_3CHO	HCHO	CH_3COOH	HCOOH	
262.2	40	22.6	10.5	6.2	0.04	27.2	0.8	67.34
265.0	34	21.8	12.5	6.6	0.08	22.4	0.7	64.08
266.5	34.5	23.7	11.2	6.0	0.05	23.8	0.6	65.35
270.5	16.5	23.6	14.0	9.7	0.05	12.5	0.5	60.35
275.0	8.5	16.5	13.1	6.8	0.10	4.9	0.3	41.70
278.0	5.25	14.6	15.4	11.1	0.60	2.2	0.3	44.20

With respect to dehydrogenation, it has been shown that ethanol vapor passed over heated copper (200-350°C.) yields acetaldehyde.[34] This catalyst containing a small amount (1 to 5 per cent) of chromium also serves in the reaction.[35]

Partial oxidation of gaseous hydrocarbon mixtures containing ethane is described by Walker.[36] He employed oxygen at elevated temperatures and pressures, and a catalyst mass consisting of aluminum phosphate and copper oxide on pumice, and obtained alcohols and aldehydes. Mixtures of gaseous saturated hydrocarbons oxidized with oxygen containing 1 per cent or less of nitric oxide (NO) at 500-800°C., using chromium, molybdenum or vanadium as catalyst, produce formaldehyde, formic acid, acetaldehyde and other products.[37] Serbinov and Neiman,[38] in the oxidation of ethane with oxygen, observed that the conversion is accelerated several-fold by the presence of small quantities of nitrogen peroxide (NO_2), but the effect was believed not to be due to direct reaction of this oxide with ethane, but rather to a transfer of energy from nitrogen peroxide to oxygen molecules.

OXIDATION OF HIGHER PARAFFIN HYDROCARBONS

Pease and Munro[39] studied the slow oxidation of propane in an attempt to ascertain the actual steps occurring. Propane-oxygen mixtures were reacted at 400°C.

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[33] D. M. Newitt and D. T. A. Townend, *Proc. World Petr. Congr.*, 1933, 2, 847; *Brit. Chem. Abs.* **B**, 1934, 823; *Chem. Abs.*, 1934, **28**, 4871.

[34] V. N. Ipatieff, *Ber.*, 1903, **36**, 1990; *Chem. Zentr.*, 1905, 1, 1002.

[35] C. O. Young, U. S. P. 1,977,750, Oct. 23, 1934, to Carbide and Carbon Chemicals Corp.; *Brit. Chem. Abs.* **B**, 1935, 894; *Chem. Abs.*, 1935, **29**, 180.

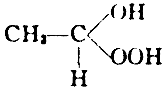
[36] J. C. Walker, U. S. P. 2,007,116, July 2, 1935, to Empire Oil & Refining Co.; *Chem. Abs.*, 1935, **29**, 5456; *Brit. Chem. Abs.* **B**, 1936, 822.

[37] French P. 788,533, 1935, to Gutehoffnungshütte Oberhausen A.-G.; *Chem. Abs.*, 1936, **30**, 1383.

[38] A. I. Serbinov and M. B. Neiman, *Compt. rend. acad. sci.* (*U.R.S.S.*), 1934, 2, 297; *Chem. Abs.*, 1934, **28**, 5320; *Brit. Chem. Abs.* **A**, 1934, 737.

[39] R. N. Pease and W. P. Munro, *J.A.C.S.*, 1934, **56**, 2034; *Chem. Abs.*, 1934, **28**, 7244; *Brit. Chem. Abs.* **A**, 1934, 1329.

and under 1 atmosphere pressure. The gases were passed through a reaction tube heated to this temperature. The tube was 1.7 cm. in diameter and 14 cm. in length, its volume being 31 cc. Contact time was kept short so as to minimize secondary oxidation. The early appearance of propene without the equivalent of hydrogen was pointed out. As secondary products, organic peroxides, aldehydes (mainly formaldehyde) and alcohols (principally methanol) represented the main portion of the substances formed. Although some of the earlier investigators[40] failed to stress the importance of peroxides as initial products, Pease and Munro found that in some instances as high as 25 moles of peroxide were formed per 100 moles of propane used. Analytical data seemed to indicate the formula



$$CH_3-CH(OH)(OOH)$$

as representing this peroxide. On decomposing, this compound gave formaldehyde. However, by coating the reaction tube with potassium chloride, peroxides were practically eliminated without materially changing the rate of oxidation. Some of their results are listed in Table 181.

TABLE 181.—*Production of Peroxides and Aldehydes.*

Temp. °C.	Ratio $C_3H_8:O_2$	Rate of Flow cc. min. 25°C. and 1 Atm.	Gases Reacted cc.		— Products Formed, cc. Gas or Vapor —							Carbon Deficiency* Per Cent
			C_3H_8	O_2	C_3H_6	C_2H_4	H_2	CO	CO_2	Perox.	Ald.	
350	1:1	100	73	161	20	6	5	60	8	18	11	10
"	"	50	87	196	20	7	7	79	10	18	20	18
400	1:3	280	20	18	6	2	5	8	1	4	—	—
"	"	50	61	141	12	5	7	67	16	15	2	12
"	"	25	67	166	11	3	14	77	21	9	—	—
400	1:1	50	109	198	28	12	5	103	15	17	4	19
400	3:1	100	67	71	28	9	5	37	4	10	7	15
"	"	50	85	99	28	11	5	49	5	7	14	26
					"KCl-Coated Tube"							
400	1:3	100	25	45	10	2	7	16	6	Trace	8	15
					Before Coating							
400	1/3	100	41	74	13	—	11	28	5	9	1	—

* In calculating this value the peroxide was considered as containing 2 carbon atoms and the aldehyde was taken as formaldehyde.

In the oxidation of propane with oxygen in a Pyrex flask (static method) Munro[41] observed the appearance of a fairly long induction period followed by a rapid reaction which was reported as being too rapid to permit precise measurement. This induction period, which was fairly reproducible, was measured as the time required for the pressure increase to build up to 5 per cent of its final value. However, when the walls of the flask were coated with potassium chloride, the pressure rose steadily, the induction period apparently being eliminated. Andreev,[42] in studying the oxidation of ethane with oxygen, found that metal wire such as gold, iron or copper lengthened an analogous induction period. Munro found further that with propane in excess the reaction started as low as 245°C., whereas, 306°C. was required for its initiation when oxygen predominated. On the other hand, Beatty and Edgar,[43] in oxidizing pure *n*-heptane with air, using the flow method, were unable to detect an induction period.

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[40] W. A. Bone and S. G. Hill, *Proc. Roy. Soc.* (London), 1930, **A129**, 434; *Brit. Chem. Abs.* **A**, 1931, 45; *Chem. Abs.*, 1931, **25**, 1360. W. A. Bone and D. T. A. Townend, "Flame and Combustion in Gases," Longmans, Green & Co., New York, 1927.

[41] W. P. Munro, *J.A.C.S.*, 1935, **57**, 1053; *Chem. Abs.*, 1935, **29**, 4999; *Brit. Chem. Abs.* **A**, 1935, 938.

[42] E. A. Andreev, *Compt. rend. acad. sci.* (*U.R.S.S.*), 1935, **1**, 610; *Chem. Abs.*, 1935, **29**, 4659; *Brit. Chem. Abs.* **A**, 1935, 830.

[43] H. A. Beatty and G. Edgar, *J.A.C.S.*, 1934, **56**, 102; *Brit. Chem. Abs.* **A**, 1934, 259; *Chem. Abs.*, 1934, **28**, 1656.

Wiezevich and Frolich[44] oxidized several of the lower paraffins (methane through heptanes), with air and oxygen, at high pressures. Among the catalysts used were calcium, chromel, silver, and aluminum. It was found that the higher members of the series were oxidized at lower temperatures than those required by the lower members. In dealing with a given hydrocarbon, it was learned also that lower pressures favored the formation of the lower alcohols and acids, whereas higher pressures gave more of the higher molecular weight products. This is best shown by runs made with pure *n*-butane. See Table 182.

TABLE 182.—*Effect of Pressure on Oxidation of Butane.*

	Per Cent of Oxygen	
Inlet Oxygen Going to:	At 33 Atm.	At 133 Atm.
Acetone	1.4	0.7
Methanol	15.0	8.4
Ethanol	2.5	6.3
Propyl alcohols	3.2	8.9
Butyl alcohols	0.6	2.5
Aldehydes	6.9	15.9
Acids	16.7	4.6
Total Useful Products	46.3	47.3

In some instances it was desired to obtain acids as main products. In such cases, the acids formed were removed (by dry lime) after each pass, the unabsorbed gases being then recirculated through the reaction chamber.[45]

It has been suggested[46] that the lower alkyl ethers, e.g., methyl or ethyl, be used as catalysts in air-oxidation of gaseous hydrocarbons such as propane. These ethers are satisfactorily employed in amounts of 1 per cent or less (on basis of hydrocarbon) and serve not only to allow oxidation to proceed at lower temperatures but also to make the velocity of reaction less susceptible to temperature variations. It is also reported[47] that alcohols, acids, aldehydes and ketones which result from the oxidation of hydrocarbons of this type (e.g., butane) may be separated from the hydrocarbon material present by extracting the mass with methanol containing water. The efficiency of the extraction is further improved by operating under superatmospheric pressures.

In the oxidation of cyclohexane with air Candea and Cristodulo[48] pointed out that this hydrocarbon favored peroxide formation more than did aromatic hydrocarbons which retarded peroxide formation and which were difficult to oxidize. In this connection may be mentioned that the oxidizability of naphthenes increases with increasing molecular weight and that their stability is further lowered by the presence of side chains.[49]

Beatty and Edgar[50] studied the oxidation of *n*-heptane as a function of temperature. The flow method was used and the reaction chamber consisted of an externally-heated Pyrex tube, 2.41 cm. in diameter and 106 cm. in length. Of this, a 65 cm. section was included in the heating zone of an electric furnace. In their experiments the pure hydrocarbon was vaporized in a current of nitrogen and later mixed with oxygen (an amount sufficient for complete combustion) so that the oxygen-nitrogen ratio was the same as that of air. The mixture was then introduced into the reaction zone, the temperatures in the various sections being measured by means of movable thermocouples. It was found that as the temperature of the gas is increased, oxidation proceeds in the following definite stages:

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[44] P. J. Wiezevich and P. K. Frolich, *Ind. Eng. Chem.*, 1934, **26**, 267; *Chem. Abs.*, 1934, **28**, 2249; *Brit. Chem. Abs.* **B**, 1934, 491.

[45] See also Chapter 42 for the production of acids from petroleum hydrocarbons.

[46] S. P. Burke and C. F. Fryling, U. S. P. 2,018,994, Oct. 29, 1935 U. S. P. 1,991,344, Feb. 12, 1935; *Chem. Abs.*, 1936, **30**, 106; 1935, **29**, 2174. Both to Doherty Research Co.

[47] P. K. Frolich and J. W. Pugh, U. S. P. 2,002,533, May 28, 1935, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1936, 584; *Chem. Abs.*, 1935, **29**, 4373.

[48] C. Candea and N. Cristodulo, *Bull. sci. ecole polytech. Timisoara*, 1934, 5, 233; *Chem. Abs.*, 1935, **29**, 8304.

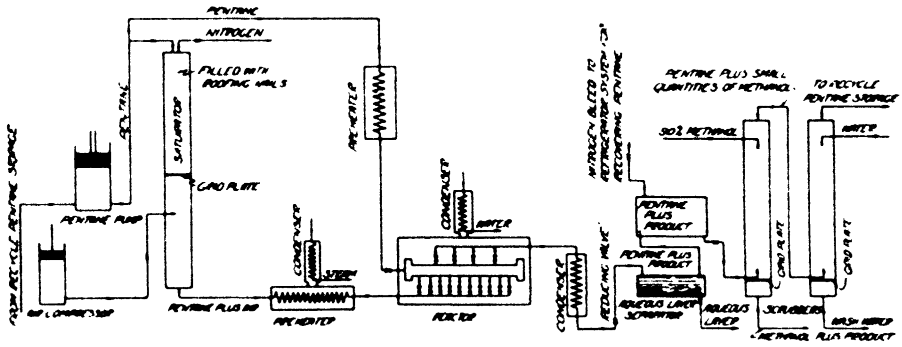
[49] N. I. Chernozhukov and S. E. Krein, *Neft. Khoz.*, 1932, **24**, 242, 285; *Chem. Abs.*, 1933, **27**, 5178.

[50] H. A. Beatty and G. Edgar, *J.A.C.S.*, 1934, **56**, 102, 107, 112; *Brit. Chem. Abs.* **A**, 1934, 259; *Chem. Abs.*, 1934, **28**, 1656.

(1) At 150-250°C. a slight reaction occurs which is possibly heterogeneous.

(2) At 250-350°C. a primary reaction takes place which is terminated within the furnace. In this step 3 moles of oxygen per mole of heptane are consumed.

(3) At 350-470°C. a subsequent reaction raises the oxygen consumption to 4.7 moles. The velocity of both the primary and subsequent reactions decreases rapidly with increasing temperature.



Courtesy Industrial and Engineering Chemistry

FIG. 202.—Flow Sheet for Pentane Oxidation. (P. J. Wiezevich and P. K. Frolich)

(4) At 470-510°C. the velocity of the primary reaction continues to decrease but the subsequent reaction is accelerated and above 490°C. the final amount of oxygen used is increased.

(5) At about 510°C. inflammation occurs.

Although the complex mixture representing the reaction products was not analyzed, it was noted that some of the intermediate products exhibited extraordinary stability toward oxygen. This followed from the fact that even though a rapid increase occurred in the total amount of oxidation between 350° and 380°C., raising the amount of oxygen used to 42.7 per cent of the final value, no change whatever occurred in the oxygen consumption from 380° to 490°C. The main reaction, which began at about 250°C. and which was believed to be of the chain-mechanism type, was accompanied by visible chemiluminescence. This continued even up to the temperature of inflammation. A similar chemiluminescence was exhibited during the oxidation of 3-heptene, although the latter was attacked at somewhat higher temperatures than the corresponding paraffin. Iso-octane (2,2,4-trimethylpentane) was found to be very inert toward oxygen and when mixed with *n*-heptane had an inhibitory effect on the oxidation of the latter. This is indeed in accord with the high antiknock value of the former material when used as fuel in gasoline engines (Chapter 44).

Aldehydes averaging eight to ten carbon atoms, and proposed for use in perfumery, have been obtained by the vapor-phase air-oxidation of a cleaner's naphtha from West Texas crude oil. Oxidation was effected using nitric acid vapor as catalyst. The best yield of aldehydes (20 per cent) was secured at 444°C., together with a 25 per cent yield of acids. The aldehydes obtained were separated from other products by means of sodium bisulphite. They possessed pleasant odors when first prepared but, when exposed to the air, soon became badly rancid, due to oxidation to the corresponding acids. No alcohols were obtained when nitric acid was employed but these did appear when small amounts of tetraethyl lead, nitrobenzene, copper oleate or benzoyl peroxide were used as catalysts.[51] Böeseken and Wildschut[52] report that benzoyl peroxide may be employed as the oxidizing agent in certain reactions. These investigators conducted experiments on the oxidation of triethylmethane, using benzoyl peroxide as the source of oxygen. Contrary to expectations, it was found that a small amount of a primary alcohol was formed, indicating that a hydrogen attached to a primary carbon of one of the methyl groups had been activated, rather than the hydrogen attached to the tertiary carbon.

In the oxidation of light paraffin oils[53] at 120°C., it was found that phosphorus pentoxide, potassium hydroxide, sodium sulphate, calcium chloride, or cupric sulphate produce little effect on the reaction. It was learned however, that when means are exerted to remove water from the mixture (e.g. by suspending dehydrating agents above the liquid), the yield of acidic products is diminished.

In a rather extended study[54] of the oxidation of hydrocarbons (boiling between 175-250°C.; sp. gr. 0.77-0.85 at 15°C.), in the vapor phase by air, it was learned that at least six reactions occur simultaneously, no catalyst being found which would sufficiently increase any one of these reactions at the expense of the others. The hydrocarbon, heated to 150°C., is mixed with a limited amount of air (previously heated to 300°C.), and passed into a reaction vessel containing the catalyst. The conditions are such that only 1-1.5 per cent of carbon monoxide and dioxide are formed. The products, recovered by condensation, consist of unsaturated and aromatic hydrocarbons, aliphatic aldehydes and ketones (saturated and unsaturated), alcohols, lactones, and small quantities of acidic compounds. The various fractions obtained have been used as odorizers (sold under the name of Detektol O. Special) for odorless gases, denaturants ("Denoxol") for alcohol, and for the prevention of deposits in coal-gas lines, and as inhibitors (known as "Denoxol-Solve") for the formation of resins and gums from unsaturates.

In nitrating a cyclopentane fraction (b.p. 50-51°C.) of a Caucasian petroleum, Markownikow[55] obtained a large yield of glutaric acid, in addition to nitrocyclopentane. Nametkin[56] obtained succinic and α-methylglutaric acids by treating cyclopentane and methylcyclopentane with nitric acid. Similarly, adipic acid has been obtained from a cyclohexane fraction.

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[51] C. Q. Sheely and W. H. King, *Ind. Eng. Chem.*, 1934, **26**, 1150; *Brit. Chem. Abs.* **A**, 1934, 1335; *Chem. Abs.*, 1935, **29**, 1061

[52] J. Böeseken and S. J. Wildschut, *Rec. trav. chim.*, 1932, **51**, 168; *Chem. Abs.*, 1932, **26**, 1233; *Brit. Chem. Abs.* **A**, 1932, 250.

[53] A. K. Plisov and E. Maleeva, *Bull. soc. chim.*, 1936, **3** (5), 1281; *Chem. Abs.*, 1936, **30**, 7995

[54] W. J. Piotrowski and J. Winkler, *Oil & Gas J.*, 1936, **25** (9), 58; *J. Inst. Pet. Tech.*, 1936, **22**, 514A.

[55] W. B. Markownikow, *Ber.* 1897, **30**, 974; *J.C.S.*, 1897, **72**, 329.

[56] S. S. Nametkin, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1603; *J.C.S.*, 1912, **102** (1), 175.

Chapter 38

Formaldehyde and Other Aldehydes

Since its discovery in the latter part of the nineteenth century as an oxidation product of methanol,[1] formaldehyde has been of ever increasing interest to chemical industry. First used as a fumigant and disinfectant, its properties of ready polymerization and a catholic willingness to condense with other substances has made it very important in the plastics industry,[2] the greatest consumer of formaldehyde at present. Although formaldehyde has a sharply irritant odor, the higher aldehydes differ in this property and some are used in the manufacture of perfumes and as solvents.[3]

Formaldehyde is generally available as the 40 per cent aqueous solution (formalin), as the solid polymer, paraformaldehyde, which deposits from the water solution, and also as the compound formed with ammonia, hexamethylenetetramine. The aldehyde is readily regenerated by heating the latter substance with acid. Another solid polymer, polyoxymethylene, is formed directly by polymerization of the liquid or gaseous monomer, sometimes with explosive violence.[4] The gaseous monomer condenses to a liquid at —19.2°C. which freezes at —118°C., according to Spence and Wild,[5] but is stable only at temperatures near that of liquid air, due to the strong tendency to form polyoxymethylene. Maintained in a solid carbon dioxide-ether bath, polymerization still proceeds to such an extent that interlocking fine crystals of the polymer convert the aldehyde to a gelatinous mass. So insoluble is this polymer in the liquid monomer, however, that no effect was discernible on the vapor pressure curve of the latter. Spence and Wild[6] believed that this polymerization of liquid formaldehyde to polyoxymethylene took place progressively from solid nuclei or solid surfaces. In an effort to test the belief, gaseous formaldehyde (obtained by heating paraformaldehyde) was specially treated to free it of any entrained solid matter. The liquid prepared by condensing this gas in a liquid air-cooled trap proved to be distinctly more stable than liquid formaldehyde prepared from gas not thus freed of solids. However, even this more stable liquid polymerized slowly from the solid surfaces of the containing vessel.

OXIDATION OF ALCOHOLS

Formaldehyde is an oxidation product of methanol, and this method of production has maintained its preeminence to the present time since the process is simple, the products readily purified, and the raw materials not costly. Oxidation of the corresponding primary alcohol is a general method for preparing formaldehyde or its higher homologues. The aldehydes can also be prepared by dehydrogenation reactions, without oxidation. Smolenski and Kowalewski[7] reported that dehydrogenation was promoted by a copper catalyst. Thus they obtained acetaldehyde by the dehydrogenation of ethyl alcohol heated in the presence of copper. Young[8] found that the copper catalyst was further activated by the addition of 1 to 5 per cent of chromium. It was prepared by impregnating a porous artificial filter stone support with mixed cupric and chromic nitrates, followed by reduction in a stream of ethyl alcohol vapor. The catalyst was then used at a temperature of 225 to 350°C., the ethyl alcohol vapors being passed over it under 0.5 to 5 atmospheres pressure. Similar dehydrogenation reactions may be carried out in the liquid phase. Thus, according to Brus,[9] anhydrous zinc sulphate reacts with ethyl alcohol, first converting it to acetaldehyde and then condensing the latter product (with loss of water) to crotonaldehyde. With *n*-propyl alcohol the action is similar, although isopropyl alcohol is dehydrogenated to acetone. The latter substance is condensed to mesityl oxide and phorone. That acetone was a primary product of dehydrogenation was confirmed by treating some of this ketone with the anhydrous sulphate and testing for mesityl oxide and phorone. Butyl alcohol is similarly converted to butyraldehyde, which in turn furnishes an iso-octenyl aldehyde. When polyhydric alcohols such as glycerol are treated in this manner, dehydration takes place, leading, in the case of glycerol, to acrolein.

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[1] A. W. Hofmann, *Ann* 1868, **145**, 357; *Ber.*, 1869, **2**, 152.

[2] See Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, **1935**.

[3] P. Shoruigin and V. Korshak, *Ber.*, 1935, **68**, 838; *Chem. Abs.*, 1935, **29**, 4736. See also French P. 779,789, 1935, to L. Givauden and Cie. Soc. anon.; *Chem. Abs.*, 1935, **29**, 5457.

[4] R. Spence and W. Wild, *J.C.S.*, **1935**, 338, 506; *Brit. Chem. Abs* **A**, 1935, 608, 691; *Chem. Abs.*, 1935, **29**, 3302, 4659.

[5] R. Spence and W. Wild, *loc. cit.* The International Critical Tables, however, list the boiling point of formaldehyde as —21°C. and the melting point as —92°C.

[6] See also J. E. Carruthers and R. G. W. Norrish, *Nature*, 1935, **135**, 582; *Brit. Chem. Abs.* **A**, 1935, 711; *Chem. Abs.*, 1935, **29**, 4100.

However, the usual procedure consists of a catalytic oxidation by air or oxygen. The importance of the reaction has led to considerable investigation of possible catalysts, and though copper, silver, or a mixed copper-silver mass is generally used,[10] various investigators have proposed oxides of molybdenum, vanadium, iron, lanthanum, thorium, neodymium, zinc or tin,[11] or certain of these substances as well as cerium, aluminum or chromium used in conjunction with electrolytic silver crystals.[12] Nevertheless, Dolgov and Bocharova,[13] after detailed experiments with synthetic methanol and air, reported that the metallic catalysts other than silver and copper were of little use. Their findings indicate that most metal oxides are not satisfactory but that a catalyst consisting of copper discs placed close together (within the reaction zone) gave a yield of 42 per cent of formaldehyde. Copper oxide with an activator such as thorium or uranium furnished yields of 21 to 42 per cent. On the other hand, Ghosh and Baksi[14] reported that cerium and thorium were advantageous promoters for copper catalyst. Ivannikov and Zherko,[15] however, working on this same problem, tested these metals and found the results disappointing. They believed that this cerium-promoted copper catalyst favored the production of methyl formate rather than formaldehyde. They also suggest that the results reported by Ghosh and Baksi may have been misleading due to the

[7] K. Smolenski and S. Kowalewski, *Bull. intern. acad. polonaise, Classe sci. math. nat.*, **1934A**, 304; *Chem. Abs.*, 1935, **29**, 1060; *Brit. Chem. Abs.* **A**, 1935, 193

[8] C. O. Young, U. S. P. 1,977,750, Oct. 23, 1934, to Carbide and Carbon Chemicals Corp.; *Chem. Abs.*, 1935, **29**, 180; *Brit. Chem. Abs.* **B**, 1935, 894.

[9] G. Brus, *Bull. soc. chim.*, 1923, **33**, 1433; *Chem. Abs.*, 1924, **18**, 613; *J.S.C.I.*, 1924, **43**, 74B.

[10] H. Dreyfus, British P. 425,550, 1935; *Chem. Abs.*, 1935, **29**, 5461; *Brit. Chem. Abs.* **B**, 1935, 443.

[11] V. E. Meharg and H. Adkins, U. S. P. 1,913,404, June 13, 1933, to Bakelite Corp.; *Brit. Chem. Abs.* **B**, 1934, 186; *Chem. Abs.*, 1933, **27**, 4252.

[12] H. A. Bond and L. B. Smith, U. S. P. 1,968,552, July 31, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 5832; *Brit. Chem. Abs.* **B**, 1935, 621.

[13] B. N. Dolgov and E. M. Bocharova, *Khim. Tverdogo Topliva*, 1932, **3**, 406; *Chem. Abs.*, 1934, **28**, 5805.

[14] J. C. Ghosh and J. B. Baksi, *Quart. J. Indian Chem. Soc.*, 1926, **3**, 415; *Chem. Abs.*, 1927, **21**, 2249.

[15] P. Y. Ivannikov and A. V. Zherko, *J. Applied Chem. (U.S.S.R.)*, 1933, **6**, 1148; *Chem. Abs.*, 1934, **28**, 4036; *Brit. Chem. Abs.* **B**, 1934, 231.

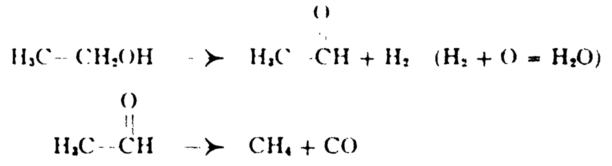
method of analysis employed, i.e., testing by gas analysis, since methyl formate and formaldehyde possess identical empirical formulas.

Gurevich and Chirvinskaya[16] found that copper gauze was the optimum catalyst, the most desirable temperature being 360°C., when the gas was composed of methanol with 52 to 57 per cent of the theoretical amount of oxygen. Under these conditions, yields of 92 to 93 per cent of formaldehyde were secured. Silver on pumice gave a 90 per cent yield, and when this metal was deposited on copper gauze, 92 per cent of the theoretical quantity was obtained. If the oxygen content of the reacting gases was increased, the yield fell rapidly. Simultaneous oxidation to carbon dioxide and formaldehyde occurred, the latter then breaking down to carbon monoxide and hydrogen. Bond and Smith[17] prepared a silver catalyst for the oxidation of methanol by forming a compacted mass of silver oxide without inert diluent and subsequently reducing this mass to silver. This was further activated by incorporation of such other metals as cerium, thorium, chromium, molybdenum, vanadium, tungsten or zinc.

In oxidizing the higher primary alcohols to the corresponding aldehydes, there is some tendency to completely oxidize off the carbinol groups with resultant degradation to the next lower aliphatic compound. Thus, Flanzy[18] reported a study of ethyl alcohol-oxidation catalyzed by copper oxide, which indicated that considerable quantities of formaldehyde were formed at 300°C. He proposed a mechanism for this reaction as follows:

$$H_3C\ \ CH_2OH \xrightarrow{\frac{1}{2}O_2} H_2C{=}CHOH + H_2O \rightleftharpoons H_2C{=} + {=}CHOH$$
$$=CHOH \longrightarrow HCHO$$

In an investigation of the oxidation of ethyl alcohol to acetaldehyde, using copper gauze as catalyst, Nikolskii[19] concluded that the process was one of dehydrogenation with subsequent oxidation of the hydrogen split off. He believed carbon monoxide to be the result of decomposition of the acetaldehyde formed, as follows:



$$H_3C{-}CH_2OH \longrightarrow H_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}H + H_2 \quad (H_2 + O = H_2O)$$
$$H_3C{-}\overset{\overset{\displaystyle O}{\|}}{C}H \longrightarrow CH_4 + CO$$

His work indicated that the reactions were due to the high temperature (600 to 700°C.) of the contact mass and the low concentration of oxygen employed. By increasing the size of the reaction chamber and reducing the catalyst temperature to 400°C., it was possible to raise the oxygen content of the entering gases to 55 or 60 per cent and to use a heavier gauge of copper gauze. This eliminated a second source of trouble, the fusion of the fine copper mesh to a sintered mass due to the heat of oxidation of hydrogen on the surface of the catalyst.

Patterson and Day[20] oxidized ethyl alcohol (with air) to acetaldehyde (using a silver catalyst) at pressures ranging from 1 to 50 atmospheres. The yield and the yield efficiency (ratio of alcohol converted to aldehyde to the total alcohol oxidized) both decreased as the pressure mounted. The data in Table 183 indicate also that considerable decomposition of intermediate products to hydrocarbon and hydrogen took place:

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[16] Z. B. Gurevich and E. Y. Chirvinskaya, *J. Chem. Ind. (Moscow)*, **1935**, No. 1, 57; *Chem. Abs.*, 1935, **29**, 3302; *Brit. Chem. Abs.* **B**, 1935, 442.

[17] H. A. Bond and L. B. Smith, U. S. P. 2,005,645, June 18, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 5124.

[18] M. Flanzy, *Compt. rend.*, 1934, **198**, 1793; *Chem. Abs.*, 1934, **28**, 5040; *Brit. Chem. Abs.* **A**, 1934, 758.

[19] M. S. Nikolakii, *Anilinokrasochnaya Prom.*, 1932, **2**, No. 4, 22; *Chem. Abs.*, 1933, **27**, 5305.

[20] J. A. Patterson and A. R. Day, *Ind. Eng. Chem.*, 1934, **26**, 1277; *Chem. Abs.*, 1935, **29**, 1059; *Brit. Chem. Abs.* **B**, 1935, 584.

TABLE 183.—*Effect of Pressure on Oxidation of Ethyl Alcohol.*

Temp. °C.	Ratio of Oxygen to Alcohol (Moles)	Alde-hyde %	Acetic Acid %	CO_2 %	CO %	Hydro-carbon %	H_2 Moles Per Mole Alcohol	Efficiency %
			Three Atmospheres Pressure					
322	0.712	37.0	2.7	11.4	6.7	2.2	.067	61.7
331	0.139	28.9	0.6	1.0	1.3	0.8	.097	88.7
			Ten Atmospheres Pressure					
330	0.238	22.7	0.6	0.5	1.3	0.8	.039	87.2
370	0.386	27.0	0.5	1.4	2.9	2.3	.191	75.0
			Twenty-Five Atmospheres Pressure					
326	0.443	14.4	1.2	2.7	1.9	6.40	.067	51.8
370	0.420	14.8	0.7	2.9	15.9	9.70	.160	32.8
			Fifty Atmospheres Pressure					
330	0.281	9.0	0.8	2.5	7.3	4.4	.062	35.0
371	0.804	3.4	0.4	16.2	26.0	15.4	.395	5.5

Butyl alcohol can be oxidized with either air or carbon dioxide, according to Rubinshtein and his associates.[21] Catalysts of chromic, manganic, ferric and vanadic oxides, precipitated silver, copper and silver-copper, and various combinations of these were tested. With air as an oxidant, a catalyst of silver (precipitated from a silver-ammonia complex by formaldehyde) mixed with 4 per cent of a copper-silver mixture was most successful, giving a yield of 68 per cent butyraldehyde with 7 per cent butyric acid at 350° to 360°C. Although less effective, ferric and vanadic oxides catalyzed the reaction at higher temperatures (400° to 550°C.), but the other metal oxides tested were useless. Vanadic oxide was reported satisfactory, however, when using carbon dioxide as the oxidizing agent, at a temperature of 550°C.

CATALYTIC OXIDATION OF HYDROCARBONS TO ALDEHYDES

Due to the large quantities of hydrocarbons available at very low cost in natural gases, interest has been aroused in catalytic oxidation producing aldehydes directly from them. Even without catalysts, the reaction takes place to a certain extent. Frear[22] investigated this action using a silica tube 1.37 cm. in diameter, the reaction being carried out at atmospheric pressure or lower, with temperatures close to 600°C. With a methane-oxygen ratio (presumably by volume) of 77 to 21 at atmospheric pressure, the formaldehyde yield increased with increasing contact time until a maximum was reached at 54 seconds. Under these conditions a 0.23 per cent yield of the aldehyde was obtained, together with 10.9 per cent carbon dioxide and 0.14 per cent of carbon monoxide. Contact times greater than 54 seconds decreased the yield and, at 103 seconds, but 0.035 per cent of formaldehyde was formed, while 13.2 per cent of carbon dioxide was produced. From these data, Frear concluded that in an unpacked silica tube the reaction is of the chain type of the 3.45 order[23] under pressures between 450 and 575 mm., the order increasing rapidly with the pressure. In a packed tube the reaction is of the first order and, at pressures below 300 mm., proceeds more rapidly than the chain mechanism.

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[21] A. M. Rubinshtein, A. A. Balandin, B. A. Dolgoploska, K. A. Morozov and L. I. Vagranskaya, *J. Applied Chem. (U.S.S.R.)*, 1933, **6**, 278; *Chem. Abs.*, 1934, **28**, 2983; *Brit. Chem. Abs.* **A**, 1933, 805.

[22] G. L. Frear, *J.A.C.S.*, 1934, **56**, 305; *Chem. Abs.*, 1934, **28**, 1916; *Brit. Chem. Abs.* **A**, 1934, 368.

[23] This fractional order number indicates that calculations based on experimentally determined re-

In industrial work, however, catalysts are almost invariably employed. In a process described by James,[24] oxygen and methane are circulated through a reaction chamber in which the "blue oxides" of molybdenum are used as catalysts. The gases then pass to a chamber in which the desired oxidation product (formaldehyde) is separated out. The unreacted gases are recirculated with the addition of fresh oxygen and methane to replace that converted. Tikhomirova and Monakhova[25] used a mixture of cracking gas and air, with a catalyst of vanadic oxide precipitated on kaolin. The reaction was carried out at 280° to 340°C., yields of from 5 to 11 per cent formaldehyde, 2 to 3.5 per cent formic acid, and 6 to 7 per cent of acetic acid being obtained. Tikhomirova[26] found that copper gauze decreased rather than increased the proportion of formaldehyde when used in conjunction with the vanadic oxide catalyst. The optimum degree of oxidation was obtained by 8 to 10 recyclings of the gaseous mixture.

Solid catalysts are not always used alone but sometimes are aided by gaseous catalysts, particularly the oxides of nitrogen.[27] As an example, the methane-oxygen mixture may have added to it less than 1 per cent of nitric oxide and the gases then passed over solid catalysts at temperatures between 600 and 700°C. The reaction may be carried out in the presence of zinc or zirconium and oxides or carbonates of such metals as aluminum, chromium, vanadium, molybdenum, tungsten, manganese, nickel or cobalt.[28]

Sheely and King[29] oxidized a cleaner's naphtha (from West Texas crude oil) in the vapor phase, using nitric acid vapor as catalyst. The best yield of aldehydes (20 per cent) containing 8 to 10 carbon atoms, along with some acids, was obtained at 444°C. The aldehydes possessed pleasant odors and were suggested for use in perfumery.

Electro-Catalytic Production of Aldehydes

Since, as already noted, oxides of nitrogen are sometimes used as catalysts in the oxidation of methane-oxygen mixtures, a number of methods have been proposed which combine the manufacture of the nitrogen oxides with their utilization in this process. Thus, Harter[30] suggested that air be blown through an electric arc causing the formation of mixed nitrogen oxides which are, however, unstable at the lower temperatures outside the arc. Methane or other hydrocarbon is blown into the apparatus to be mixed with the stream of unstable and decomposing nitrogen oxides escaping from the immediate region of the arc. The decomposition of the oxides releases oxygen in a highly activated form so that the hydrocarbon is oxidized at comparatively low temperatures, e.g., 100 to 500°C. Under these

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action velocity constants showed the series of reactions proceeded at a rate less than that of a third order reaction, though greater than that of a fourth order reaction. For a discussion of reaction orders, see Chapter 20.

[24] J. H. James, U. S. P. 1,941,010, Dec. 26, 1933, to C. P. Byrnes; *Brit. Chem. Abs.* **B**, 1934, 918; *Chem. Abs.*, 1934, **28**, 1354.

[25] M. M. Tikhomirova and V. Monakhova, *Azer. Neft. Khoz.*, 1935, No. 6, 79; *Chem. Abs.*, 1936, **30**, 3986.

[26] M. M. Tikhomirova, *Azer. Neft. Khoz.*, 1934, No. 10, 82; *Chem. Abs.*, 1935, **29**, 6033

[27] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

[28] British P. 433,559, 1934, to Gutehoffnungshutte Oberhausen A. G.; *J. Inst. Pet. Tech.*, 1935, **21**, 424A; *Brit. Chem. Abs.* **B**, 1935, 939; British P. 448,733, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 411A.

[29] C. O. Sheely and W. H. King, *Ind. Eng. Chem.*, 1934, **26**, 1150; *Chem. Abs.*, 1935, **29**, 1061; *Brit. Chem. Abs.* **A**, 1934, 1335.

[30] H. Harter, U. S. P. 1,985,875, Dec. 25, 1934; *Chem. Abs.*, 1935, **29**, 1103; *Brit. Chem. Abs.* **B**, 1935, 1130.

conditions the partial oxidation products are relatively stable. "Bleaching earths," silica gel, or metallic catalysts may be used as additional catalysts to direct the oxidation to the formation of formaldehyde. A method described by Nashan[31] uses an undamped, visible discharge of high-tension, high-frequency alternating current as the activating agent. In this case the nitrogen oxides produced are somewhat more stable and react with the hydrocarbon (methane, for instance) to produce partial oxidation products, but also a quantity of the nitrogen is sufficiently activated to further react with some of the formaldehyde produced. The products of this process include not only formaldehyde, but also hexamethylenetetramine, which can be recovered by solvent extraction and recrystallization. Nashan[32] also reported that oxygen may be used as the oxidizing agent in such a high-frequency, high-tension field if less than atmospheric pressure is applied. If methane is used as the hydrocarbon, a good yield of formaldehyde is obtained. Fujimoto[33] found that a similar mixture produced dihydroxydimethylperoxide ($HOCH_2OOCH_2OH$) when treated with the silent electric discharge. This compound is fairly stable, but breaks down on heating with or without a catalyst (platinum black or zinc may be used) to yield formaldehyde, formic acid, acetaldehyde and methyl alcohol.

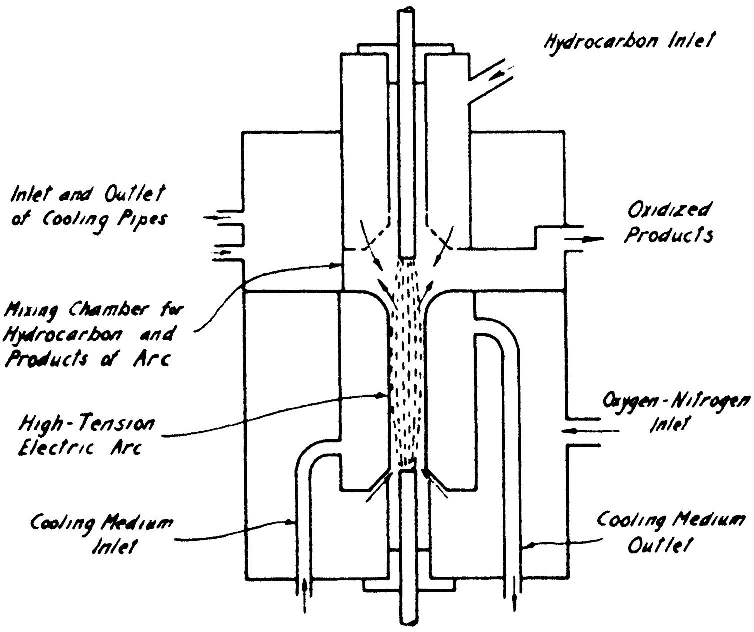
Hydrocarbon Inlet
Inlet and Outlet of Cooling Pipes
Oxidized Products
Mixing Chamber for Hydrocarbon and Products of Arc
Oxygen-Nitrogen Inlet
High-Tension Electric Arc
Cooling Medium Inlet
Cooling Medium Outlet

FIG. 203.—Oxidation of Hydrocarbon Gases with Nitrogen Oxides Formed in Electric Arc. (H. Harter)

Not only can the electric discharge bring about combination of hydrocarbons with oxygen, but carbon dioxide may be used as the oxidizing agent in the discharge. Finlayson and Plant[34] reported a method for the production of acetaldehyde and formaldehyde based on the oxidation of methane by means of carbon dioxide. The gaseous mixture was passed through an electric discharge supplied with alternating current at a frequency of about 1000 cycles. Other investigators have shown that by varying the proportions of methane to carbon dioxide, the products are accordingly varied. Thus, if an excess of methane is present, the reaction tends to produce acetaldehyde,[35] but if the carbon dioxide concentration is equal to or greater than the methane concentration, the product is principally formaldehyde.[36]

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[31] P. Nashan, U. S. P. 1,930,210, Oct. 10, 1933, to Gutehoffnungshutte Oberhausen A.-G.; *Chem. Abs.*, 1934, **28**, 2280.

[32] P. Nashan, U. S. P. 1,909,215, May 16, 1933, to Gutehoffnungshütte Oberhausen A.-G.; *Chem. Abs.*, 1933, **27**, 3675.

[33] H. Fujimoto, Japanese P. 109,412, 1935, to Minister of the Navy; *Chem. Abs.*, 1935, **29**, 3691.

Fester and Schivazappa[37] investigated the electrolytic reduction of carbon monoxide and concluded from their results that only traces of formaldehyde are formed in this manner, since this lower oxide of carbon is not a true unsaturated compound. However, they believed that a combination of catalytic and electrolytic reduction in solution should give determinable amounts of the aldehyde, and this conclusion was verified by experiments. Very small quantities of formic acid and methyl alcohol were formed simultaneously.

DECOMPOSITION OF ALDEHYDES

The high temperatures used in the catalytic oxidations of the gaseous hydrocarbons to aldehydes lead to considerable decomposition of the desired products. Spence[38] finds that formaldehyde, for instance, reacts rapidly with oxygen in a Pyrex tube at 317°C. In an unpacked tube, the products are largely carbon monoxide and water, but in a tube packed with powdered glass, carbon dioxide and water are produced. In addition to loss of product through such oxidation as this, purely thermal decomposition is a considerable factor. The mechanism of this decomposition has been studied in a number of ways. Patat and Sachsse[39] took advantage of the fact that atomic hydrogen is a catalyst for the conversion of parahydrogen to orthohydrogen in tracing the reaction.[40] In this way it was possible to show that no more than very minute quantities of free hydrogen radicals could be present. Tests were made using formaldehyde and parahydrogen heated together at a temperature of 823°C. A total pressure of 625 mm. was used, 600 mm. due to parahydrogen and 25 mm. pressure of formaldehyde. No decrease in the concentration of parahydrogen was detected. Work with formic acid (20 mm. partial pressure) and parahydrogen (760 mm.) heated together at 300 to 440°C. gave similar negative results. It was concluded from the data that the decomposition of such methyl compounds proceeds through saturated substances. The same investigators also report that the free-radical, or chain mechanism, cannot be applicable in these decompositions. The parahydrogen results indicate so low a concentration of free hydrogen atoms that an improbably high heat of activation (29,000 cal.) must be postulated to account for the acetaldehyde decomposition on the basis of a chain reaction. Winkler and Hinshelwood[41] arrived at a similar conclusion from investigations of the effect of surface-volume ratios on reaction speed. Results obtained from operations at a temperature of 562°C. and an initial pressure of 240 mm. gave no evidence that the decomposition of acetaldehyde was heterogeneous or depended on a chain reaction. Staveley and Hinshelwood[42] have shown that sufficient nitric oxide (NO) may accelerate the decomposition of acetaldehyde, although smaller amounts do not have this effect; neither do small percentages inhibit the decomposition. On the other hand, partial pressures of nitric oxide in the range near 2 mm. do act to inhibit the decomposition of propionaldehyde. However, increasing the amount of nitric oxide present diminishes this effect, until a positive catalytic effect is finally exerted when large proportions of the nitrogen compound are present. The investigators believe that the decomposition of the latter aldehyde involves a short (2 unit) chain reaction, although the decomposition of acetaldehyde involves no chain mechanism.

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[34] D. Finlayson and J. H. G. Plant, U. S. P. 1,986,885, June 8, 1935, to Celanese Corp.; *Chem. Abs.*, 1935, **29**, 1021.

[35] German P. 600,040, 1934, to Gutehoffnungshütte Oberhausen A.-G.; *Chem. Abs.*, 1934, **28**, 6376.

[36] German P. 580,580, 1933, to Gutehoffnungshütte Oberhausen A.-G.; *Chem. Abs.*, 1934, **28**, 979

[37] G. Fester and M. Schivazappa, *Rev. facultad quim. Argentina*, 1934, **22**, 238B; *Chem. Abs.*, 1935, **29**, 5359.

[38] R. Spence, *J.C.S.*, 1936, 649; *Brit. Chem. Abs.* **A**, 1936, 801; *Chem. Abs.*, 1936, **30**, 6631.

[39] F. Patat and H. Sachsse, *Nachr. Ges. Wiss. Gottingen, Math.-physik. Klasse*, Fachgruppe III, 1935, **1**, 41; *Chem. Abs.*, 1935, **29**, 6878; and *Naturwiss.*, 1935, **23**, 247; *Brit. Chem. Abs.* **B**, 1935, 708; *Chem. Abs.*, 1935, **29**, 5072.

[40] The parahydrogen molecule differs from the orthohydrogen molecule in that the proton spin of the two hydrogen atoms forming the ortho molecule is in the same direction; in the para molecule the two protons spin in opposing directions. The two forms of the molecule differ in various physical properties, such as specific heat and thermal conductivity. Normal hydrogen gas contains both forms in ratio of 1 parahydrogen to 3 orthohydrogen molecules, according to K. F. Bonhoeffer and P. Harteck (*Naturwissenschaften*, 1929, 17, 182; *Chem. Abs.*, 1929, **23**, 2614.). Practically pure parahydrogen can be prepared by adsorption on activated carbon at liquid hydrogen temperatures. So prepared, the para molecules are sufficiently stable to remain practically unchanged for a week at room temperature. Hydrogen atoms, platinum black, and certain other substances catalyze the conversion to the 1 to 3 equilibrium mixture nearly instantaneously.

A number of substances frequently present as intermediates in the production of aldehydes from hydrocarbons by oxidation are catalysts for the decomposition of aldehydes. Letort[43] reports that traces of oxygen act in this manner at temperatures in the range of 477°C. Fletcher[44] found that ethylene oxide in small quantities induces a decomposition of acetaldehyde below 500°C. The conversion is proportional to the square root of the ethylene oxide pressure and to slightly less than the first power of the acetaldehyde pressure. Decomposition is retarded by the presence of diluent gases (e.g., helium), but the course of the reaction is unchanged. According to Verhoek[45] nitrous oxide also exerts a catalytic effect on the decomposition. In this case, there appears to be a reaction between the aldehyde and the nitrogen oxide to produce a substance which is the active catalyst or the initiator of a chain reaction. In a clean silica bulb, the catalyzed reaction is of the first order with respect to acetaldehyde. Letort[46] finds that carbon monoxide and methane exert a retarding effect on the decomposition of acetaldehyde, and although there appears to be both an activating and deactivating effect, the latter greatly predominates. The presence and accumulation of these products retard the decomposition reaction in such a way that, though it starts as a mechanism of the 1.5 order, during the course of the action, the order number rises to 1.8.

RECOVERY AND REMOVAL OF ALDEHYDES

The direct concentration of formaldehyde solutions is difficult due to the formation of azeotropic mixtures and the tendency to precipitate the polymer, paraformaldehyde.[47] Korzhev and Rossinskaya[48] report that formaldehyde forms an azeotropic mixture with water in 11 to 12 per cent aqueous solutions. At concentrations above 12 per cent, the proportion of formaldehyde in the vapor is less than that in the initial solution, and the aldehyde accumulates in the solution. If there is less than 8 or 9 per cent of formaldehyde in the solution, distillation yields a product richer in the aldehyde. These investigators postulate an equilibrium between formalin hydrate [$CH_2(OH)_2$], paraformaldehyde [$(CH_2O)_n$] and formaldehyde. When distillation is carried out under reduced pressure, the concentration of formaldehyde in the vapor decreases while that in the residue increases. Korzhev, Frolova and Rossinskaya[49] found that if crude dilute formaldehyde is made neutral with calcium hydroxide and the water distilled off at 30 mm. pressure (conditions under which the aldehyde does not go over), the distillation can be completed at atmospheric pressure to give a 37 per cent solution. From a 13 per cent formaldehyde solution a concentrated distillate may be obtained by adding calcium chloride to make a 33 per cent brine, and distilling at atmospheric pressure. Hasche[50] reports a similar distillation, adding that substances capable of raising the boiling point of the solution sufficiently to decompose the polymers of formaldehyde will permit distillation of concentrated solutions. He suggests the chlorides of magnesium and zinc as well as that of calcium.

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[41] C. A. Winkler and C. N. Hinshelwood, *Proc Roy. Soc.* (London), 1935, **A149**, 355; *Chem. Abs.*, 1935, **29**, 4243; *Brit. Chem. Abs.* **A**, 1935, 827.

[42] L. A. K. Staveley and C. N. Hinshelwood, *J.C.S.*, **1936**, 812, *Chem. Abs.*, 1936, **30**, 6631; *Brit. Chem. Abs.* **A**, 1939, 939

[43] M. Letort, *Compt. rend.*, 1935, **200**, 312; *Chem. Abs.*, 1935, **29**, 2059; *Brit Chem Abs* **A**, 1935, 307.

[44] C. J. M. Fletcher, *J.A.C.S.*, 1936, **58**, 534; *Chem. Abs.*, 1936, **30**, 2922; *Brit. Chem Abs.* **A**, 1936, 570.

[45] F. H. Verhoek, *Trans. Faraday Soc.*, 1935, **31**, 1527; *Brit Chem Abs* **A**, 1935, 1466.

[46] M. Letort, *Compt. rend.*, 1936, **202**, 491; *Brit. Chem. Abs.* **A**, 1936, 707; *Chem Abs.*, 1936, **30**, 2471.

[47] However, W. S. Hinegardner (U. S. P. 2,002,243, May 21, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 4381) reports that water solutions of formaldehyde are made more stable by the addition of 5 to 10 per cent of hydrogen sulphide. A reversible reaction takes place between the aldehyde and the sulphide, preventing precipitation of polymers. The sulphur compound is most stable at lower (0 to 5°C.) temperatures when the aldehyde is least stable

[48] P. P. Korzhev and I. M. Rossinskaya, *J. Chem Ind.* (Moscow), 1935, **12**, 610; *Chem Abs.*, 1935, **29**, 7941; *Brit. Chem Abs.* **B**, 1936, 10.

REACTIONS OF ALDEHYDES

The carbonyl group of the aldehydes is typified by its high reactivity,[51] and although a detailed discussion of the aldehyde reactions is beyond the scope of the present text, some mention of the more important reactions must be made. According to Richter[51a], the high reactivity of the aldehydes places them among the most important substances for purposes of synthesis. An aldehyde is readily converted to the corresponding carboxylic acid, on oxidation, and consequently serves as a powerful reducing agent. Thus if acetaldehyde and air (an excess of oxygen being avoided) are passed over an oxidation catalyst at 40 to 70°C. under 50 to 100 pounds per square inch pressure, the corresponding acid, acetic acid, is formed. If dry gases are used, and a dehydrating agent is present during the reaction, acetic anhydride is also obtained. It is reported that an acetate, butyrate or propionate of manganese serves as a catalyst in this reaction, and may be mixed with an activator such as copper, nickel or cobalt acetates. In producing the anhydride, the aldehyde is oxidized to an extent of about 70 per cent, then the gases are cooled quickly to 20°C.[52] If an aldehyde is warmed with a dilute ammoniacal silver solution, silver is precipitated in the form of a mirror on the walls of the containing vessel. In the presence of nascent hydrogen, however, the aldehydes readily reduce to the corresponding primary alcohol. With acid anhydrides, the aldehydes react to form esters of the hydrated form of the aldehyde, the α, α-glycol:

$$R-CHO + (R'CO)_2O \longrightarrow R-CH(O-COR')_2$$

The aldehydes react with ammonia to form aldehyde-ammonias which are readily soluble in water but rather unstable, breaking down in the presence of acids to yield the original components. Pyridine bases are produced when these aldehyde-ammonias are heated. When an aldehyde is warmed with an aqueous solution of hydroxylamine, aldoximes of well defined properties are formed which are frequently helpful in identifying a particular aldehyde. With acetaldehyde, acetoxime is formed:

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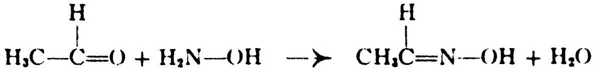
[49] P. P. Korzhev, P. A. Frolova and I. M. Rossinskaya, *J. Chem. Ind.* (*Moscow*), 1935, **12**, 721; *Brit. Chem. Abs.* **B**, 1936, 10.

[50] R. L. Hasche, U. S. P. 2,015,180, Sept. 24, 1935, to A. O. Smith Corp.; *Chem. Abs.*, 1935, **29**, 7346; *Brit. Chem. Abs.* **B**, 1936, 920.

[51] Although it is not easy to absorb phosgene rapidly, the formaldehyde derivative, the hexamethylenetetramine, was found to be one of the most effective agents for the rapid and complete absorption required in gas masks, according to S. J. M. Auld (*Ind. Eng. Chem.*, 1918, **10**, 297, *Chem. Abs.*, 1918, **12**, 1017).

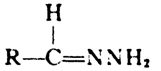
[51a] Richter-Anschütz, "Chemie der Kohlenstoffverbindungen," edited by R. Anschutz, Akademische Verlagsgesellschaft m.b.H., Leipzig, 1928, 1, 247.

[52] British P. 446,259, 1936, to Shawinigan Chemicals Ltd.; *Chem. Abs.*, 1936, **30**, 6765; *Brit. Chem. Abs.* **B**, 1936, 920.



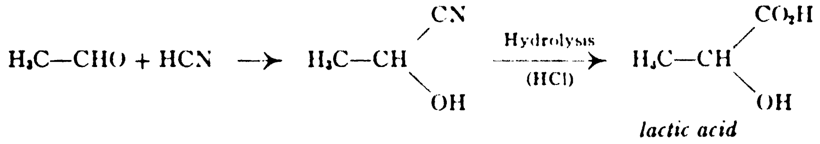
$$H_3C-\overset{\overset{H}{|}}{C}=O + H_2N-OH \longrightarrow CH_3\overset{\overset{H}{|}}{C}=N-OH + H_2O$$

Hydrazine reacts similarly with aldehydes to produce compounds of the type



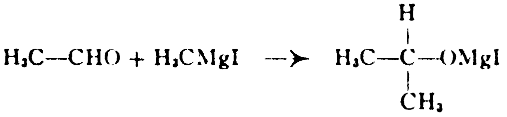
$$R-\overset{\overset{H}{|}}{C}=NNH_2$$

With hydrogen cyanide, a reaction takes place yielding cyanohydrins, nitriles of α-hydroxyacids. These cyanohydrins can be converted to the acids by means of hydrochloric acid:



With ammonium cyanide, aldehydes react to form the nitriles of α-amino acids, which, when treated with hydrochloric acid, yield the amino acids.

The aldehydes are also able to react with Grignard reagents:



$$H_3C-CHO + H_3CMgI \longrightarrow H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-OMgI$$

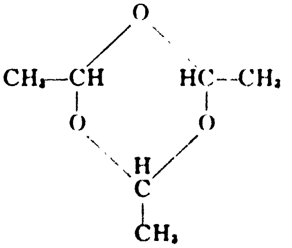
The reaction product yields secondary alcohols on hydrolysis with water or acids.

Under suitable conditions (e.g., in the presence of zinc chloride) aldehydes undergo a type of condensation whereby two or more aldehyde molecules become linked:

$$H_3C-CHO + H_3C-CHO \longrightarrow H_3C-CH(OH)CH_2CHO$$

A similar reaction can take place between two different aldehydes.[53]

Aldehydes polymerize in the presence of alkalies to form aldehyde-resins, a reaction characteristic of all the aliphatic aldehydes save formaldehyde. With acids, however, the polymerization is of a different nature, leading to the formation of paraldehyde, in the case of acetaldehyde, with the strong evolution of heat. The vapor pressure and density data indicate that the composition corresponds to $(C_2H_4O)_3$. Paraldehyde does not show the reactions characteristic of the carbonyl group but probably has the structure,



with linkage taking place through the oxygen atoms.

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[53] V. von Richter, "Organic Chemistry," English Edition (Third) by E. N. Allott, Kegan Paul, Trench, Trubner & Co., London, 1934.

The study of the aldehydes has been made more difficult in some cases by the readiness with which these substances polymerize forming hydrates and condensation products. Reiche and Meister[54] found that ether solutions of formaldehyde, prepared by shaking ether with 40 per cent aqueous solutions of the aldehyde, did not contain free HCHO, but instead, the hydrate $CH_2(OH)_2$. They reported that solutions prepared in this manner are stable for weeks, deposit no polymers on long standing, and have only a faint odor. On the other hand, a solution prepared by passing gaseous formaldehyde into ether has a powerful, extremely penetrating odor, and continuously precipitates polymeric formaldehyde. This polymerization takes place so rapidly that the concentration of the monomer is reduced to 50 per cent of its original value in even a few hours. An ether solution of anhydrous formaldehyde (prepared from dry ether and gaseous aldehyde) reacts with hydrogen peroxide to produce hydroxy-methyl-hydroperoxide ($HO\text{-}CH_2\text{-}OOH$) as a relatively stable oil which is not sensitive to friction but which explodes violently when heated in a flame. With alkali the peroxide compound yields 97 per cent formic acid and evolves hydrogen and oxygen. With ferrous sulphate, a reaction takes place yielding 50 per cent formic acid and 50 per cent formaldehyde. Briner and Lardon[55] report a study of the ozonization of the lower aliphatic aldehydes in solution in water, carbon tetrachloride and hexane. Ozonization of acetaldehyde, propionaldehyde or butyraldehyde in each of the solvents showed a marked increase in the ratio of moles of oxygen fixed to moles of ozone consumed as the series was ascended. The increase is more marked with aldehydes of higher molecular weight. Very little autoxidation of the aldehydes was found to take place in water solution, but the solvent involved had pronounced effect on the way in which the oxygen of ozone was fixed in the molecule. Thus, in carbon tetrachloride, most of the combined oxygen went to form the corresponding acid from the aldehyde. In the cyclohexane solutions, large proportions of peracid were formed. Formaldehyde differed from the higher aldehydes in that it was only slightly attacked by ozone, either in the solvents or in the gaseous state.

Krauskopf and Rollefson[56] studied the photochemical reaction between chlorine and gaseous formaldehyde and found that a small amount of formyl chloride can be prepared. The two gases were reacted in a quartz bulb (and in later tests in a tube spiraled about a 300 watt tungsten lamp) and then led to a liquid air trap where the condensible reaction products (largely hydrogen chloride) were frozen out. Carbon monoxide was pumped off from the trap. Fractional distillation and extractions of the condensed material concentrated the formyl chloride produced. This substance is highly unstable and breaks down very rapidly at room temperature to yield carbon monoxide and hydrogen chloride, making it impossible to get a purified sample of the material. It was found that in water the reaction likewise produced the monoxide and hydrochloric acid, with no tendency to hydrolyze to formic acid. It was possible, however, to prepare the derivative *assym*-formo-*m*-xylidide, melting at 114 to 115°C. Although formyl chloride is stable only at the temperature of liquid air, formyl fluoride prepared by Nesmejanow and Kahn[57] (by reacting formic acid and potassium fluoride in benzyl chloride or trichlorophenylmethane solution) was fairly stable at room temperature, decomposing only after 4 hours or so. The fluoride, moreover, does hydrolyze to formic acid.

Hexamethylenetetramine, $(CH_2)_6N_4$, obtained by the reaction of formaldehyde and ammonia, readily regenerates formaldehyde on treatment with an acid. The. structure of this compound is not definitely known, and Dominikiewicz[58] proposes a structure basing his conclusions largely on the results of various benzoylation reactions. With acetic anhydride in cold ethyl ether, hexamethylenetetramine yields:

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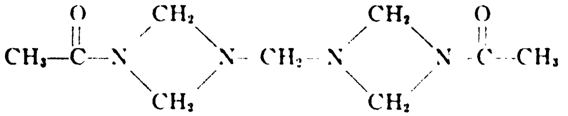
[54] A. Reiche and R. Meister, *Ber.*, 1935, **68**, 1465; *Brit. Chem. Abs.* **A**, 1935, 1222; *Chem. Abs.*, 1935, **29**, 6877.

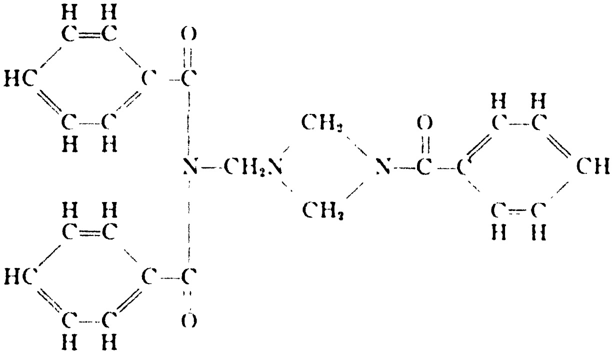
[55] E. Briner and A. Lardon, *Helv. Chim. Acta.*, 1936, **19**, 850; *Chem. Abs.*, **1936**, 30, 6277.

[56] K. B. Krauskopf and G. K. Rollefson, *J.A.C.S.*, 1934, **56**, 2542; *Chem. Abs.*, 1935, **29**, 685; *Brit. Chem. Abs.* **A**, 1935, 177.

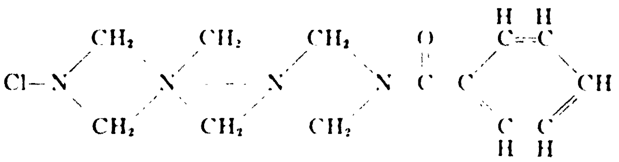
[57] A. N. Nesmejanow and E. J. Kahn, *Ber.*, 1934, **67**, 370; *Chem. Abs.*, 1934, **28**, 3053; *Brit. Chem. Abs.* **A**, 1935, 509.



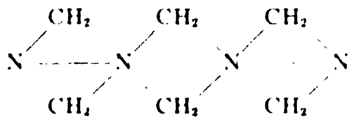
An analogous di-benzoyl derivative cannot be prepared, due to the further benzoylation to trimethylenetribenzoyltriamine:



A further benzoylation product of similar structure containing four benzoyl groups, dimethylene-N,N′-bismethylenedibenzoylaminediamine, can also be prepared. Benzoylation of hexamethylenetetramine in chloroform in the presence of pyridine gives chloro-benzoylhexamethylenetetramine:



On the basis of these and certain other experiments, the formula



is attributed to hexamethylenetetramine.[59]

Aldehydes also react fairly readily with aliphatic nitro compounds to give nitro-alcohols and glycols. This type of reaction is discussed more fully in another section, however.[60]

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[58] M. Dominikiewicz, *Arch Chem Farm*, 1935, **2**, 78; *Chem Abs*, 1936, **30**, 1029.

[59] The aldehydes undergo many reactions resulting in the formation of useful resins, but this is beyond the scope of the present text. For discussion of this material see Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

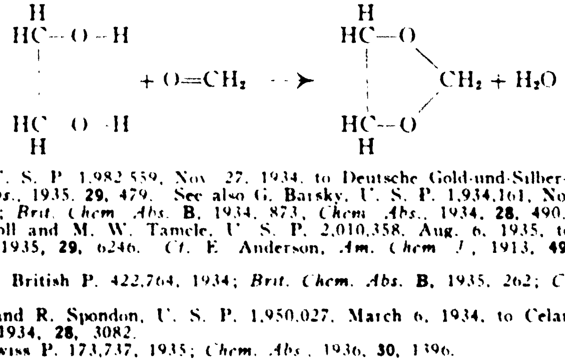
[60] See Chapter 47.

UTILIZATIONS OF THE ALDEHYDES

As has been noted, various higher oxidation products such as carboxylic acids can be produced from aldehydes. Wiesler[61] oxidized acetaldehyde in the liquid phase (at 55° to 80°C.) to acetic acid. The oxidation of higher iso-aldehydes to produce the corresponding iso-acids has been described by Groll and Tamele.[62] Moskovits[63] carried out the oxidation of aldehydes in the presence of an alcohol and obtained 91 per cent yields of the corresponding esters. Acetic acid can be produced from formaldehyde at 300-400°C., according to Green and Spondon.[64] In this case 100 atmosphere pressure is used to bring about the condensation.

The aldehydes will polymerize or condense with themselves readily. Hoffer[65] reports forming unsaturated high molecular weight aldehydes from lower saturated aldehydes by using a secondary organic base or its salt as catalyst. Various formals (and mixed formals) can be prepared by direct reaction of different alcohols with formaldehyde.[66] The higher formals, such as those formed from dodecyl or cetyl alcohol, produce readily emulsified materials useful in treating textiles.[67]

The lower aldehydes can be made to yield those of greater molecular weight by using the aldol condensation as an intermediate step. According to Kagan and his associates[68] acetaldehyde in the presence of 2 per cent alkali solution condenses to yield 97 per cent of the theoretical quantity of crotonaldehyde. This latter product was hydrogenated in the vapor phase (using a copper catalyst) to obtain butyraldehyde and butanol. Reduction of an aldehyde by means of aluminum isopropoxide, $[(CH_3)_2CH\text{-}O\text{-}]_3Al$, produces the corresponding alcohol, Young, Hartung and Crossley report.[69] They have obtained butanol from butyraldehyde by this means. Reduction of the condensation product of the reaction of aldehydes will yield alcohols of high molecular weight. Thus, butyraldehyde and heptadecaldehyde undergo an aldol-like condensation in the presence of secondary amines such as diethylamine. The product of this condensation can be hydrogenated (with catalysts such as nickel) to produce higher mono- and polyhydroxy alcohols (e.g., octyl alcohol).[70] The condensation of lower polyhydroxy alcohols (such as ethylene glycol) with aldehydes yields distillable diethers:



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[61] K. Wiesler, U. S. P. 1,982,559, Nov. 27, 1934, to Deutsche Gold-und-Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1935, **29**, 479. See also G. Barsky, U. S. P. 1,934,161, Nov. 7, 1933, to American Cyanamid Co.; *Brit. Chem. Abs.* **B**, 1934, 873, *Chem. Abs.*, 1934, **28**, 490.

[62] H. P. A. Groll and M. W. Tamele, U. S. P. 2,010,358, Aug. 6, 1935, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 6246. *Cf.* E. Anderson, *Am. Chem. J.*, 1913, **49**, 179; *Chem. Abs.*, 1913, **7**, 1701.

[63] N. Moskovits, British P. 422,764, 1934; *Brit. Chem. Abs.* **B**, 1935, 262; *Chem. Abs.*, 1935, **29**, 4374.

[64] S. J. Green and R. Spondon, U. S. P. 1,950,027, March 6, 1934, to Celanese Corp. of America; *Chem. Abs.*, 1934, **28**, 3082.

[65] M. Hoffer, Swiss P. 173,737, 1935; *Chem. Abs.*, 1936, **30**, 1396.

[66] H. Wuyts and P. Docquier, *Bull. soc. chim. Belg.*, 1935, **44**, 297; *Brit. Chem. Abs.* **A, 1935**, 1104; *Chem. Abs.*, 1936, **30**, 430. See also G. W. Seymour, U. S. P. 2,036,304, April 7, 1936, to Celanese Corp. of America; *Chem. Abs.*, 1936, **30**, 3440.

[67] H. Flesch, C. Flesch and L. E. Abelmann, British P. 425,396, 1934; *Brit. Chem. Abs.* **B**, 1935, 442; *Chem. Abs.*, 1935, **29**, 5457.

[68] M.-Y. Kagan, G. D. Lyubarskii and S. F. Fedorov, *J. Applied Chem. (Russia)*, 1934, **7**, 135; *Chem. Abs.*, 1935, **29**, 452.

[69] W. G. Young, W. H. Hartung and F. S. Crossley, *J. A. C. S.*, 1936, **58**, 100; *Chem. Abs.*, 1936, **30**, 1737.

[70] British P. 433,869, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1935, 938.

Dreyfus[71] reports that this reaction is catalyzed by the presence of pyrosulphates or pyrophosphates.

As has been pointed out, one important reaction of formaldehyde in industry is that of its condensation with various other substances (e.g., phenols, urea, casein) in making synthetic plastics.[72]

The separation of the complex mixture of products resulting from oxidation of petroleum, representing practically all stages of oxidation, presents considerable difficulties. Ellis[73] suggested a means of direct utilization of these products which does not require their separation. Inasmuch as the greatest demand for aldehydic materials is in the plastics industry, the petroleum aldehydes present can be directly separated by their condensation to a synthetic resin. One hundred and fifty parts of a mixture of oxidation products containing 27 per cent formaldehyde, 3 per cent acetaldehyde and considerable methanol along with a small proportion of ethanol was reacted with 60 parts of urea. A material was produced which was white, plaster-like and practically odorless. Resins can also be obtained by condensations of the aldehydes with phenols, thiourea or ammonium thiocyanate. During the oxidation of petroleum to produce aldehydes, there is simultaneously formed a gummy, semi-resinous mass of higher molecular weight oxidation products. Ellis has shown that this tarry complex possesses phenolic properties and suggests that these substances be condensed with the simultaneously produced petroleum aldehydes. The material resulting is a hard, infusible, insoluble resin which may be employed in molding or coating compositions.

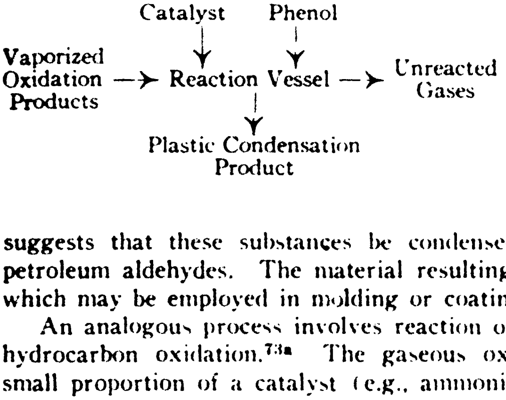

FIG. 203A. Flow Chart for Reaction of Phenols with Aldehydic Hydrocarbon Oxidation Products. (O. R. Sweeney, F. C. Vilbrandt, H. H. Beeson and H. A. Montgomery)

An analogous process involves reaction of phenols with aldehydes obtained by hydrocarbon oxidation.[73a] The gaseous oxidation products are mixed with a small proportion of a catalyst (e.g., ammonia) and contacted with phenol, either molten, vaporized or in solution, reaction taking place at 50-150°C. In this manner bodies of an aldehydic character are removed as a plastic condensation product, leaving as unreacted material vapors consisting essentially of alcohols and ketones.

Uses have been developed for the aldehydes or their polymers without combination with other substances. There has been some interest in the possibilities inherent in the polymerization of the higher aldehydes to synthetic resins.[74]

According to van der Wal[75] aldehydes materially improve the characteristics of pickling solutions used in cleaning metals. Aldehyde polymers of various types are employed, as well as hexamethylenetetramine.[76] The ability of formaldehyde to precipitate proteins is important in making waterproof glues, coating materials and cements.[77] By treating bone or skin glue with formaldehyde and adding the product to cement, the tightness is considerably increased.[78] If phosphorus-containing proteins are treated with formaldehyde, a product capable of stabilizing bituminous emulsions is formed.[79] An emulsifying agent giving soap-like reactions, capable of splitting fats, and forming solutions which foam readily on shaking can be prepared by condensing formaldehyde with a strongly basic non-aromatic amine (such as diethyl amine) and a substituted phenol such as α,α,γ,γ-tetramethylbutylphenol.[80]

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[71] H. Dreyfus, U. S. P. 2,045,843, June 30, 1936; *Chem. Abs.*, 1936, **30**, 5590.

[72] See Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[73] Carleton Ellis, U. S. P. 1,952,060, March 27, 1934, to Ellis-Foster Co.; *Brit. Chem. Abs.* **B**, 1935, 112; *Chem. Abs.*, 1934, **28**, 3606. U. S. P. 2,043,992, June 16, 1936, to Ellis-Foster Co.; *Chem. Abs.*, 1936, **30**, 5327.

[73a] O. R. Sweeney, F. C. Vilbrandt, H. H. Beeson and H. A. Montgomery, U. S. P. 2,024,954, Dec. 17, 1935, to Hanlon Buchanan, Inc.; *Chem. Abs.*, 1936, **30**, 1065; *Brit. Chem. Abs.* **B**, 1937, 16.

[74] Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935, Chapter 23.

[75] M. J. van der Wal, *Chem. Weekblad.*, 1935, **32**, 709; *Brit. Chem. Abs.* **B**, 1936, 200.

[76] *Cf.* D. H. Tompkins, U. S. P. 1,961,652, June 5, 1934, to Rubber Service Labs. Co.; *Brit. Chem. Abs.* **B**, 1935, 907; *Chem. Abs.*, 1934, **28**, 4693. F. B. Downing and R. G. Clarkson, U. S. P.

Osburn and Lipp[81] report that acetaldehyde at 75°F. is an effective insecticide in destroying the Japanese Beetle (in fruit). It may be employed in concentrations of the order of 2 pounds per 1000 cu. ft. in air. Flach[82] reports that vaporized aldehydes are capable of preventing loss of water in stored fruits and vegetables. He recommends a concentration of 0.05 per cent of formaldehyde at 0°C.

2,006,710, July 2, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 5411; *Brit. Chem. Abs.* **B**, 1936, 796. British P. 414,404, 1934, to Soc. pour l'ind. chim. a Bale; *Chem. Abs.*, 1935, **29**, 475; *Brit. Chem. Abs.* **B**, 1934, 873.

[77] H. Werde, U. S. P. 1,981,405, Nov. 20, 1934, to Paterson Parchment Paper Co.; *Chem. Abs.*, 1935, **29**, 604; *Brit. Chem. Abs.* **B**, 1935, 990.

[78] French P. 769,986, 1934, to Epidos Soc. anon.; *Chem. Abs.*, 1935, **29**, 573.

[79] German P. 604,328, 1934, to Deutsche Vialit G.m.b.H.; *J. Inst. Pet. Tech.*, 1935, **21**, 140A.

[80] H. A. Bruson, U. S. P. 2,033,092, March 3, 1936, to Röhm and Hass Co.; *Chem. Abs.*, 1936, **30**, 2669.

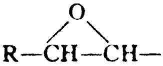
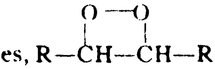
[81] M. R. Osburn and J. W. Lipp, *U. S. Dept. of Agri. Circ.*, **1935**, 373; *Chem. Abs.*, 1936, **30**, 4611.

[82] J. Flach, German P. 603,055, 1934; *Chem. Abs.*, 1935, **29**, 519.

Chapter 39

Oxidation of Unsaturated Hydrocarbons

FORMATION OF UNSATURATED HYDROCARBONS

In general, the olefins react more readily with oxygen than do the corresponding saturated hydrocarbons. However, oxidation does not necessarily split the molecule at the double bond but may proceed so as to give intermediate products such as epoxides,  $R{-}\overset{\diagup O \diagdown}{CH{-}CH}{-}R'$, peroxides,  $R{-}\overset{O{-}O}{\overset{|\quad\;|}{CH{-}CH}}{-}R'$, glycols or acids. (Note: R and R′ may be hydrocarbon radicals or hydrogen atoms, etc.)

The major source of olefinic compounds is the cracking of petroleum hydrocarbons, and this source alone supplies the demand almost completely. They can be produced, however, by partial oxidation of the corresponding saturated hydrocarbons. These oxidations are, necessarily, more accurately controlled than those designed to produce the oxy-compounds and are typified by high temperatures and small amounts of oxygen.[1] Thus, one suggested process involves heating the saturated hydrocarbon (methane) under atmospheric pressure to a temperature of 1200°C. with a small amount of oxygen.[2] Under reduced pressure, the hydrocarbons may be heated with more than 10 per cent of oxygen (presumably by volume) but less than the amount required for complete oxidation.[3] Nitrogen oxides (NO_2, for example) which supply free oxygen at the high temperatures employed, may serve as the oxidizing agent used in converting saturated hydrocarbons to olefins, it is reported. The temperatures recommended in these processes are almost invariably high (in the neighborhood of 1000°C.). The oxygen content of the final mixture should range between 10 and 45 per cent by volume.[4] Winkler and Feiler[5] report that in general, in order to convert methane to acetylene, the hydrocarbon must be preheated to 1000-1200°C. or higher. Gases containing large proportions of methane mixed with its homologues (as in coke-oven gas) require temperatures in the range 800 to 900°C., but if the starting paraffinic hydrocarbon is largely propane and butane, a temperature of 500 to 800°C. is usually sufficient. The reaction tubes should be constructed of materials which will minimize deposition of carbon. These investigators suggest carbon silicide or other silicides for this purpose. In an example, 10 liters per hour of oxygen and 20 liters per hour of a mixture of methane homologues (ethane, 14 per cent, propane, 51 per cent, and butane, 12 per cent) were passed separately through heated silica tubes 2 mm. in diameter. Both the oxygen and the hydrocarbon mixture were preheated to about 700°C., the hydrocarbons being thus converted to olefins to the extent of about 36 per cent. The juncture of the heated oxygen with the olefin-containing hydrocarbon gas produced a short, extremely hot flame. The reaction gases escaped through an attached silica tube (2 mm. in diameter) at a very high velocity. The reacted gases were of the following composition:

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[1] R. N. Pease and J. M. Morton (*J.A.C.S.*, 1933, **55**, 3190; *Chem. Abs.*, 1933, **27**, 4992; *Brit. Chem. Abs.* **A**, 1933, 1017) report that thermal decomposition of the hydrocarbons tends to crack first the paraffins, the olefins being more resistant. High temperatures increase the tendency toward olefin formation while the presence of oxygen prevents accumulation of hydrogen.

[2] French P. 754,000, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1046.

[3] French P. 792,101, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 4175.

[4] British P. 447,470, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1936, 778; *J. Inst. Pet. Tech.*, 1936, **22**, 439A.

[5] F. Winkler and P. Feiler, U. S. P. 1,995,136, March 19, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 2972.

Gas	*Per Cent*
Carbon dioxide	2.0
Acetylene	11.0
Ethylene	9.8
Carbon monoxide	10.0
Hydrogen	30.5
Methane	33.5
Nitrogen (present originally as impurity in the hydrocarbon gases)	3.2

OXIDATION OF OLEFINS

Dreyfus[6] reports that the degree to which an olefin is oxidized may be controlled by governing the conditions of the reaction zone and by lengthening or shortening the time of contact. For the production of ethylene oxide with a minimum of higher oxides, the optimum conditions are mild temperatures, short contact times, and employment of a catalyst having a basic reaction. A diluent such as carbon dioxide or nitrogen aids in suppressing the higher oxides, and ammonia or other volatile bases can be added to maintain the basic catalytic conditions. The production of acetaldehyde is favored by hydration catalysts such as phosphoric acid or zinc chloride at temperatures of 300 to 400°C. Acetic acid is the principal product if an excess of oxygen is used at relatively high temperatures with an active oxidation catalyst such as silver, copper, or their oxides.

Lefort[7] produced ethylene oxide, however, using temperatures from 150 to 400°C. and a powerful oxidation catalyst such as silver activated by copper, iron or gold. The reaction he proposes employs oxygen and steam as the oxidizing agents. Lenher[8] reports that the reaction producing ethylene oxide from ethylene by oxidation with oxygen is influenced by the surface of the reactor. The process can be carried on to some extent in a reaction vessel having a surface-to-volume ratio of not more than 4 to 1. The mixed gases are led through a packed-tube preheater where they are heated to 450°C. in contact with 4-mesh broken Pyrex glass. The effect of great surface-volume ratio in this preheater is to inhibit reaction almost completely, and the heated gases are then led into the reaction chamber proper which fulfills the requirement of low surface-to-volume ratio (Fig. 204). Here the reaction is said to proceed to yield about 20 per cent ethylene oxide, 65 per cent formaldehyde and acetaldehyde, and 3.2 per cent formic acid.

The ready reactivity of the double bond makes it possible to carry out a type of additive oxidation using substances other than the usual oxidizing agents. Carbon dioxide, and even carbon monoxide, normally a reducing agent, have been used with good results. Thus, Ramage,[9] using carbon dioxide and steam in the presence of an iron catalyst, produced alcohols from olefins. Larson[10] reports that carbon monoxide and ethylene can be combined in the presence of an acid catalyst, such as hydrochloric acid. The presence of oxygen in the reactants, however, leads to corrosion of the apparatus and deactivation of the catalyst, and tends to cause polymerization of the olefin. To remove the oxygen, this investigator proposes that the gases be passed through a solution made up of sodium anthraquinone-2-sulphonate, sodium hyposulphite and 30 per cent aqueous sodium hydroxide. In an analogous reaction, Carpenter[11] uses an inert diluent, such as nitrogen, and the mixture of ethylene, steam and carbon monoxide is reacted at 375°C. in the presence of phosphoric, boric or arsenic acid deposited on charcoal. Carpenter[12] also found that the undiluted gases can be reacted in the presence of acid salts such as zinc hydrogen phosphate or calcium dihydrogen phosphate [$Ca(H_2PO_4)_2$] or similar tungstic, molybdic or uranic salts. The reaction takes place at 325 to 350°C. under 200 to 700 atmospheres pressure. This ethylene-carbon monoxide-steam reaction to yield acids has been effected with other catalysts, e.g., chloroacetic acid,[13] silico-tungstic acid,[14] barium chloride,[15] carbon tetrachloride and activated carbon,[16] or activated carbon alone,[17] or by having the reaction take place in a chamber which is made of a 90 per cent silver alloy.[18] The reaction is aided also by leading the gases (under 700 atmospheres pressure) over a salt such as potassium carbonate which will react with the acid produced. A temperature of about 300°C. is recommended[19] in this operation.

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[6] H. Dreyfus, British P. 397,161, 1933, *Chem. Abs.*, 1934, **28**, 777, *Brit. Chem. Abs.* **B**, 1933, 903.

[7] T. E. Lefort, U. S. P. 1,998,878, April 23, 1935, to Soc. francaise de catalyse generalisee; *Chem. Abs.*, 1935, **29**, 4029.

[8] S. Lenher, U. S. P. 1,995,991, March 26, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 3350. Canadian P. 352,120, 1935; *Chem. Abs.*, 1935, **29**, 7342. British P. 400,297, 1933, *Chem. Abs.*, 1934, **28**, 2012, *Brit. Chem. Abs.* **B**, 1934, 10.

[9] A. S. Ramage, U. S. P. 2,035,189, March 24, 1936, to M. Wiley and O. L. Smith, trustees; *Chem. Abs.*, 1936, **30**, 2985.

[10] A. T. Larson, U. S. P. 1,994,955, March 19, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 2975; *Brit. Chem. Abs.* **B**, 1936, 264.

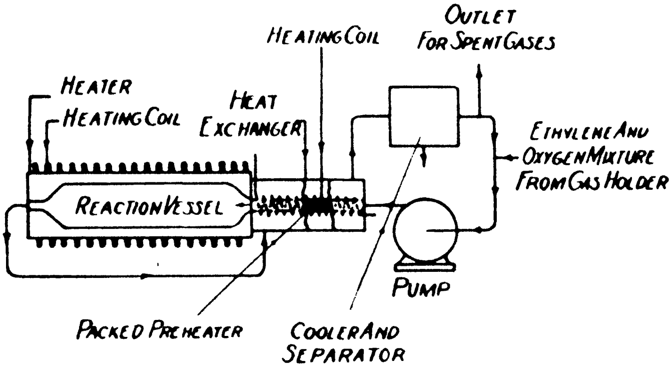

FIG. 204.—Diagram of Apparatus for Direct Oxidation of Olefins. (S. Lenher)

If aqueous alkali metal hydroxide is used, propene as well as ethylene can be made to combine directly with the hydroxide to form the metal acetate. Britton, Nutting and Huscher[20] suggest that the reaction in this case is:

$$CH_3CH{=}CH_2 + KOH + H_2O \longrightarrow CH_3COOK + CH_4 + H_2$$

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[11] G. B. Carpenter, U. S. P. 2,015,065, Sept. 24, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 7345.

[12] G. B. Carpenter, U. S. P. 1,981,081, Nov. 20, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 939.

[13] J. C. Woodhouse, U. S. P. 2,025,677, Dec. 24, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 1070.

[14] A. T. Larson, U. S. P. 2,022,244, Nov. 26, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 736.

[15] G. B. Carpenter, U. S. P. 1,957,939, May 8, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 262; *Chem. Abs.*, 1934, **28**, 4071.

[16] A. T. Larson, U. S. P. 2,020,689, Nov. 12, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 491.

[17] W. E. Vail, U. S. P. 1,979,717, Nov. 6, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 181; *Brit. Chem. Abs.* **B**, 1935, 893.

[18] W. E. Vail, U. S. P. 2,033,161, March 10, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 2992.

[19] W. E. Vail, U. S. P. 2,000,053, May 7, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1936, 488; *Chem. Abs.*, 1935, **29**, 4027.

[20] E. C. Britton, H. S. Nutting and M. E. Huscher, U. S. P. 2,000,878, May 7, 1935, to Dow Chemical Co.; *Chem. Abs.*, 1935, **29**, 4026.

Carried out at 365 to 375°C., the yield is said to be 30 per cent. In addition, a certain amount of isopropyl alcohol and polymers of propene are formed. Basic aluminum salts (e.g., potassium aluminate) act as catalysts in this reaction.

It has been proposed also that the oxidation be carried out in liquid medium. Whitmore, Homeyer and Trent[21] produced *ter*-butylacetic acid by passing diisobutylene through sodium dichromate and sulphuric acid and further oxidizing this intermediate product with a hypohalite such as sodium hypochlorite. Selenium dioxide reacts with cyclo-olefins to produce ketones, according to Schwenk and Borgwardt.[22] The reaction is carried out in solution under pressure. Thus l-menthene in ethyl alcohol is reacted with selenium dioxide to give an 85 per cent yield of a ketomenthene of the formula $C_{10}H_{16}O$. Riley[23] reports that the lower olefins (ethylene, propene, butene and amylene) react with selenium dioxide to form glyoxals or glyoxal polymers. The reaction takes place very readily, starting at temperatures as low as 50°C., and this investigator recommends 300°C. as the upper limit for successful reaction to form these substances.

Hydrogen peroxide effects oxidation of the double bond in a different way, in general leading to a hydroxylation, according to Milas and Sussman.[24] These investigators report that anhydrous hydrogen peroxide is stable in tertiary butyl alcohol for considerable periods, and can be kept for 6 months or longer at room temperature with little decomposition. The reagent was prepared by mixing the tertiary alcohol (400 cc.) with 100 cc. of 30 per cent hydrogen peroxide, and adding anhydrous sodium sulphate to bring about separation of water. The alcohol layer contained most of the peroxide and was further dried by anhydrous calcium sulphate. The addition of osmium tetroxide to the reagent thus prepared made it a highly active oxidizing agent which readily converted isobutene to isobutene glycol, trimethylethylene to trimethylethylene glycol, allyl alcohol to glycerol, and several of the unsaturated acids to the corresponding dihydroxy acids. As an example of the latter reaction, cinnamic acid was converted into phenylglyceric acid. From cyclohexene these investigators obtained adipic acid. On the other hand, Dupont and Dulou[25] were able to oxidize cyclohexene to cyclohexanediol. Quite similar to this method of oxidizing olefins is the procedure of Criegee,[26] who employed diethyl ether in place of butanol as reaction medium. The latter investigator, however, obtained aldehydes as main products. As an example of this oxidation, stilbene yielded benzaldehyde.

Ellis[27] has proposed that the mixed olefinic materials of the acid extract from cracked gasoline be treated with dilute nitric acid to effect the oxidation. The olefinic extract was added drop by drop to nitric acid (of 1.3 specific gravity). Considerable heat was generated by the oxidation, and the temperature was maintained between 30° and 40°C. Distillation of the oxidized material yielded first a light yellow, inflammable oil. This readily dissolved nitrocellulose, and its reaction with sodium sulphite solution indicated the presence of ketone material. The heavy end of the distillate was a darker oil, considerably less inflammable, and containing no appreciable amount of ketonic material. It was, however, found to be a fairly good solvent for celluloid. Pirlet[28] has suggested that nitrogen oxides be used as the oxygen carriers in oxidizing olefins.

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[21] F. C. Whitmore A. H. Homeyer and W. R. Trent, U. S. P. 2,004,066, June 4, 1935, to Mallinckrodt Chemical Works; *Brit. Chem Abs* **B**, 1936, 920; *Chem. Abs.*, 1935, **29**, 4776.

[22] E. Schwenk and E. Borgwardt, German P. 584,373, 1933, to Schering-Kahlbaum A.-G.; *Chem. Abs.*, 1934, **28**, 1356. See also British P. 403,838, 1933, to Schering-Kahlbaum A.-G.; *Brit. Chem Abs.* **B**, 1934, 355.

[23] H. L. Riley, U. S. P. 1,999,576, April 30, 1935, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1935, **29**, 4029.

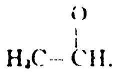
[24] N. A. Milas and S. Sussman, *J.A.C.S.*, 1936, **58**, 1302; *Chem. Abs.*, 1936, **30**, 5940; *Brit. Chem. Abs.* **A**, 1936, 1091.

[25] G. Dupont and R. Dulou, *Compt. rend.*, 1936, **203**, 92; *Chem. Abs.*, 1936, **30**, 8179

[26] R. Criegee, *Ann.*, 1936, **522**, 75; *Chem. Abs.*, 1936, **30**, 3811.

[27] Carleton Ellis, U. S. P. 1,418,368, June 6, 1922, to S. B. Hunt; *Chem. Abs.*, 1922, **16**, 2695; *J.S.C.I.*, 1922, **41**, 567A.

THE MECHANISM OF ETHYLENE OXIDATION

Vaidya[29] has investigated the destructive oxidation of ethylene in flames by spectroscopic methods, and bands were found which indicated that CH and OH radicals were present. A system of fainter bands was investigated and tentatively assigned to HCO, though there is a possibility they result from a nitrogen-oxygen compound formed from the air in which the hydrocarbon burned. In the slow combustion of ethylene under atmospheric pressure at 300°C., Bone, Haffner and Rance[30] have found evidence that the process is a homogeneous reaction preceded by a definite induction period. During this induction period a small amount of aldehyde appears, but no peroxide. Experiments with the addition of nitric oxide or acetaldehyde as catalyst, along with oxygen, showed that as little as 1 per cent of the former substances eliminated the induction period and accelerated the subsequent reaction. Formaldehyde, although it shortens the induction period, does not affect the velocity of the final reaction. Ethylene oxide, on the other hand, has no effect on the induction period but retards the rate of reaction. Of the ethylene-oxygen mixtures tested, the most reactive proved to be one of 2 volumes of ethylene to 1 of oxygen, which gave ethylene oxide as the first product. It was concluded that the reaction proceeds as a series of hydroxylations, vinyl alcohol, $H_2C=CHOH$, being formed in the first step; this is transformed rapidly into an equilibrium mixture of the three C_2H_4O isomerides vinyl alcohol, ethylene oxide, and acetaldehyde,  $H_3C{-}\overset{O}{\overset{|}{C}}H$. Water vapor was found not to affect either the induction period or the rate of reaction appreciably. On the other hand, Steacie and Plewes[31] report a study of the effect of acetaldehyde on the oxidation mechanism of ethylene in which they found that the oxidation was not influenced by the presence of the aldehyde, and concluded that acetaldehyde was unimportant in the chain propagation of oxidation in ethylene-oxygen mixtures. Bone and Bell[32] made further investigations on the effects of water vapor on the slow combustion of ethylene-oxygen mixtures, and reached the conclusion that the oxidation is direct, with no intervention of steam. The gases were dried by treatment with phosphorus pentoxide, and the evidence tended to show that this intensive drying increased rather than diminished the reactivity of the gas mixtures both in slow and in explosive combustion.

Other oxidations of ethylene have been investigated, involving the presence of oxidants other than oxygen. Steacie and McDonald[33] tested the oxidizing properties of nitrous oxide atmospheres and believe that while this gas supports flame combustion, the nitrogen compound itself does not act as the oxidizing agent. On the other hand, it was believed that the decomposition product, atomic oxygen, was the active substance. It was found that ethylene-nitrous oxide mixtures had a higher ignition temperature than did ethylene-oxygen compositions. The latter mixtures react at a measurable rate at 300° to 450°C., although the nitrous oxide-ethylene reaction was slow even at 530°C. The latter reaction seemed to be an indirect oxidation of the polymerization and decomposition products of ethylene.

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[28] G. Pirlet, Belgian P. 412,497, 1935, *Chem Abs.*, 1936, **30**, 5588

[29] W. M. Vaidya, *Proc. Roy. Soc.*, 1935, **147A**, 513; *Chem. Abs.*, 1935, **29**, 1324; *Brit. Chem. Abs.* **A**, 1935, 279.

[30] W. A. Bone, A. E. Haffner and H. F. Rance, *Proc. Roy. Soc.*, 1933, **143A**, 16; *Brit. Chem. Abs.* **A**, 1934, 151; *Chem. Abs.*, 1934, **28**, 1252.

[31] E. W. R. Steacie and A. C. Plewes, *Proc. Roy. Soc.*, 1934, **146A**, 72; *Brit. Chem. Abs.* **A**, 1934, 1179; *Chem. Abs.*, 1934, **28**, 6613.

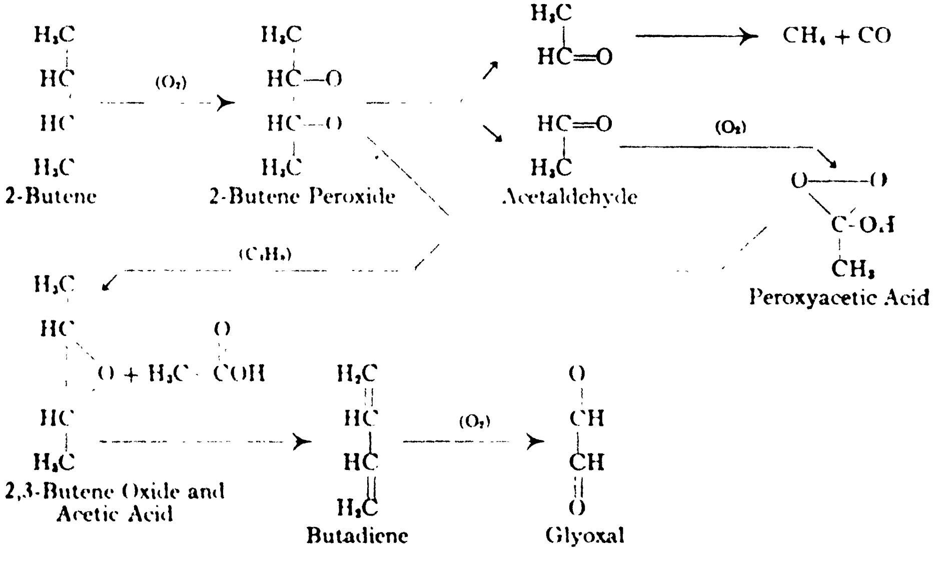
[32] W. A. Bone and J. Bell, *Proc. Roy. Soc.*, 1934, **144A**, 257; *Brit. Chem. Abs.* **A**, 1934, 1603; *Chem. Abs.*, 1934, **28**, 4580.

[33] E. W. R. Steacie and R. D. McDonald, *Can. J. Research*, 1935, **12**, 711; *Brit. Chem. Abs.* **A**, 1935, 1213; *Chem Abs.*, 1935, **29**, 5727.

Barkhash[34] reports that although hydrogen peroxide does not ordinarily react with ethylene or pentene at room temperature, the addition of ferrous sulphate catalyzes the reaction and a mixture is formed, from which acetone, carbon dioxide, formic acid and acetic acid have been isolated. Aldehydes and higher homologues of acetone, propionic acid and glycols were not found, however.[35]

Oxidation Mechanism of Higher Olefins

Lucas, Prater and Morris[36] have attempted to determine the oxidation mechanism of 2-butene, as a typical example of the unsaturated hydrocarbons. If hydroxylation takes place at either of the two unsaturated carbon atoms, methyl ethyl ketone would be a reaction product. On the other hand, if oxidation occurs at both carbon atoms, dimethyl glycolic aldehyde or dimethyl glyoxal should result. When a mixture of 2-butene and oxygen (with the hydrocarbon in excess) was passed through a Pyrex tube at 375 to 490°C., the principal reaction products were acetaldehyde and butadiene. Other substances were also identified among the products. These included glyoxal, an olefin oxide, an acid and some peroxide. They believed that hydroxylation is not important, since no methyl ethyl ketone is formed. A reaction mechanism was proposed, as follows:



The butene, in addition, showed a tendency to polymerize to octene at the higher temperatures employed (490°C.).

Steacie, Hatcher and Horwood[37] studied the decomposition of glyoxal at temperatures between 410 and 450°C. and found that the substance disintegrates according to a first-order homogeneous reaction. Considerable carbon and tar were formed, and the results were erratic. They believed the transformation occurred about equally in three ways:

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[34] A. P. Barkhash, *J. Gen. Chem.* (*U.S.S.R.*), 1935, **5**, 254; *Chem. Abs.*, 1935, **29**, 5067; *Brit. Chem. Abs.* **A**, 1935, 957.

[35] On the other hand, Carius (*Ann.*, 1863, **126**, 210; *Beilstein*, 1918, **1**, 183) reported that ethylene reacts with hydrogen peroxide to yield a small quantity of glycol.

[36] H. J. Lucas, A. N. Prater and R. E. Morris, *J.A.C.S.*, 1935, **57**, 723; *J. Inst. Pet. Tech.*, 1935, **21**, 160A; *Chem. Abs.*, 1935, **29**, 3649.

[37] E. W. R. Steacie, W. H. Hatcher and J. F. Horwood, *J. Chem. Physics*, 1935, **3**, 291; *Chem. Abs.*, 1935, **29**, 4246; *Brit. Chem. Abs.* **A**, 1935, 827.

$$
\begin{aligned}
&(1)\quad \mathrm{OHC{-}CHO} \longrightarrow 2\mathrm{CO} + \mathrm{H_2} \\
&(2)\quad \mathrm{OHC{-}CHO} \longrightarrow \mathrm{C} + \mathrm{CO} + \mathrm{H_2O} \\
&(3)\quad \mathrm{OHC{-}CHO} \longrightarrow (\mathrm{OHC{-}CHO})_n,\ \text{(a tarry polymer)}
\end{aligned}
$$

They concluded that simple mechanisms previously suggested for the glyoxal decomposition were incorrect.

Hock and Schrader[38] found that two moles of cyclohexene take up 0.4 mole of oxygen in the course of 150 to 200 hours when exposed to light, about 20 per cent of the theoretical quantity for saturation. They report that the addition of a small quantity of eosin catalyzes the reaction so that it then proceeds at twice the former rate. Fractional distillation under reduced pressure yields, besides unchanged cyclohexene, as much as 19 per cent of the peroxide, $C_6H_{10}O_2$, and about 2 per cent of a peroxidic residue of a viscous, tarry nature. The cyclohexene peroxide dissolves (to the extent of about 5 per cent) in cold water to give a weakly acidic reaction. The solution becomes turbid on heating due to a reversible hydration reaction. In cold water, the peroxide adds water to form $C_6H_{10}(OH)(OOH)$, a substance which is unstable at the higher temperatures. If the 5 per cent aqueous solution is distilled under high vacuum, 2 per cent of the peroxide is recovered in the distillate. By titrating the distillate with stannous chloride-hydrochloric acid and ferric chloride solution, it was found that the dried distillate was 96 per cent peroxide. Heated with 2N sulphuric acid, the peroxide yields 50 per cent of *cis*-cyclohexane-1,2-diol and 10 to 20 per cent of cyclopentenealdehyde. Dissolved in cold sodium hydroxide and heated to 50°C. it yielded 60 to 65 per cent of 1-cyclohexene-3-ol. This same product can be formed by reducing the peroxide in aqueous sodium sulphite.

The photo-activation of olefin oxidation is of some technical interest, in that considerable amounts of unsaturated hydrocarbons are generally present in the oil sprays used in curbing insect pests on plants. Tucker[39] conducted a series of experiments which showed that the unsaturated substances are not toxic to foliage, but that the acidic substances formed by their oxidation are. At ordinary temperatures this slow oxidation takes place at a measurable rate only under the influence of light, and his experiments demonstrated that apricot leaves were not damaged by the oils when kept in the dark. However, a few days' exposure to the light brought about formation of "asphaltogenic acids" which were destructive. This investigator found that the presence of more than 0.5 per cent of these acids produced symptoms of poisoning. It was suggested that the acidic substances pass through the osmotic membranes of the cell walls of the leaf comparatively readily and break down within the cell to form colloidal asphaltic particles.

Despite the foregoing, Beatty and Edgar[40] reported that olefins do not always absorb oxygen more readily than do the corresponding paraffins. Under the conditions of their experiments, working with *n*-heptane, 1-heptene and 3-heptene, the data showed that heptane oxidized most readily of the three, 1-heptene next, and 3-heptene oxidized most slowly. A Pyrex glass furnace was used, the volatile fuel being mixed (in 2 per cent concentration) with air. The furnace was not

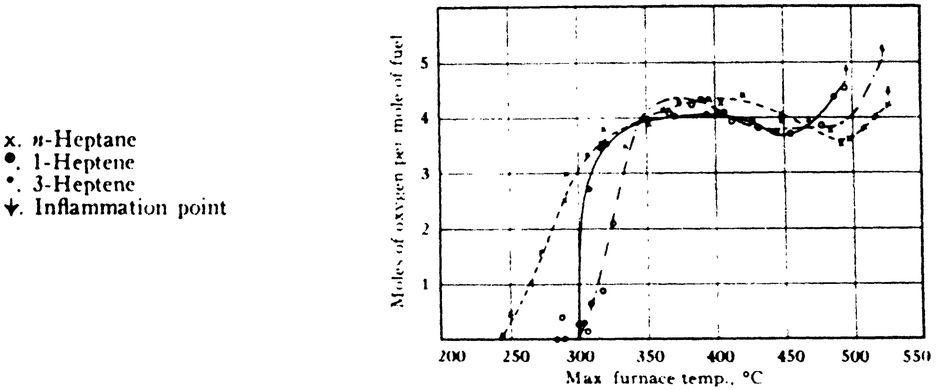
[38] H. Hock and O. Schrader, *Naturwissenschaften*, 1936, **24**, 159; *Chem. Abs.*, 1936, **30**, 4472; *Brit. Chem. Abs.* **A**, 1936, 603.

[39] R. P. Tucker, *Ind. Eng. Chem.*, 1936, **28**, 459; *Chem. Abs.*, 1936, **30**, 3575; *J. Inst. Pet. Tech.*, 1936, **22**, 272A. See also Chapter 51.

[40] H. A. Beatty and G. Edgar, *J.A.C.S.*, 1934, **56**, 107; *Chem Abs.*, 1934, **28**, 1656; *Brit. Chem. Abs.* **A**, 1934, 259.

run at steady temperature but was arranged in such a way that the temperature rose throughout the experiments at a rate of 2°C. per minute. Under these conditions, *n*-heptane began to oxidize at 244°C., the two heptenes at about 300°C. The maximum oxygen absorption was about 40 per cent of the theoretical in the case of each of the hydrocarbons, though the rate of oxidation varied widely. It was found, too, that there is a negative temperature coefficient of reaction velocity at higher temperatures (400° to 450° or 500°C.). The temperatures of inflammation, however, were not in the same order as the reaction velocities, that is, the l-heptene ignited most readily (at approximately 490°C.), the 3-heptene at approximately the same temperature that the *n*-heptane inflamed, 525°C. (See Fig. 205.)

Pigulevskii[41] investigated the oxidation of acetaldehyde and benzaldehyde, separately, in the presence of octene, and found that the latter acted as an inhibitor, or protector. Atmospheric oxygen was used, and although the oxidation of the aldehydes was inhibited, either of these substances acted as an activator in the oxidation of the unsaturated hydrocarbon. In studying the mechanism of these oxidations, the investigator found that peroxy-benzoic and peroxy-acetic acids, intermediates in the oxidation of benzaldehyde and acetaldehyde, respectively were active agents in oxidizing octene to octene oxide. Peroxyacetic acid oxidized octene more rapidly than it did acetaldehyde.



Courtesy Journal of American Chemical Society

FIG. 205.—Relative Amount of Oxidation of Heptane and Heptenes as a Function of Temperature. (H. A. Beatty and G. Edgar)

The frequent experience that platinum oxide catalysts used in hydrogenating olefins must occasionally be shaken with air or oxygen in order to reactivate them is due, according to Thomson,[42] to the stimulating effects of olefin dioxides and other oxidation products formed. It has been generally found that pure olefinic material cannot be hydrogenated by a catalyst contaminated by traces of iron, but that impure olefins can be reduced when using such a poisoned catalyst. The experiments conducted showed that the reactivating effect was due to the acid oxidation products formed during the shaking with air, or to those present in the impure olefinic material. It is known that these substances oxidize readily in air, and an experiment was conducted in which trimethylethylene, freshly distilled over sodium, was hydrogenated by an iron-poisoned catalyst. It was found that the reaction stopped after 27 per cent of the theoretical amount of hydrogen had been absorbed. The percentage reduction could be increased by shaking the olefin, not the catalyst, with air or oxygen. The introduction of 0.001 mole of furoyl, benzoyl or succinyl peroxide reduced the time for 90 per cent reduction to roughly 40 or 50 per cent of the original time. The investigator believed that these peroxides were reduced to the corresponding acids, and it was found, in fact, that 0.002 mole of furoic, benzoic or succinic acid had an equally marked effect.

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[41] V. V. Pigulevskii, *J. Gen. Chem.* (*U.S.S.R.*), 1934, **4**, 616; *Chem. Abs.*, 1935, **29**, 2145; *Brit Chem. Abs.* **A**, 1934, 1329.

[42] G. Thomson, *J.A.C.S.*, 1934, **56**, 2744; *Chem. Abs.*, 1935, **29**, 723; *Brit. Chem. Abs.* **A**, 1935, 192.

Various per-acids actively oxidize unsaturated compounds at the double bond, though the rates of reaction vary widely. Thus, Stuurman[43] reports that the reaction velocities of the lower olefins with peracetic acid range as follows:

Olefin	*Relative Reaction Velocity*
Ethylene	0.19
Propene	4.20
2-Butene	93.00
Isobutene	92.00
1-Pentene	4.30
2-Pentene	95.00
2-Methylbutene-2	1240.00
Cyclopentene	195.00
Methylcyclopentene	2220.00
Cyclohexene	129.00

Böeseken[44] and associates note that the rate of oxidation with peracetic acid is greatly influenced by the structural relationship between the alkyl groups and the double bond. Heptene-1 is much more slowly oxidized by peracetic acid than heptene-3 or 2-methylhexene-1. Diallyl is relatively slowly oxidized. Diolefins such as isoprene (2-methyl-1,3-butadiene) absorb the first oxygen atom very rapidly, but the second oxygen atom is taken up comparatively slowly. It was also reported that the velocity constant for the oxidation of ethylene by peracetic acid was almost too small to measure, but that of tetramethylethylene and peracetic acid was too great to be measured. The activating effect of alkyl groups introduced on the double-bonded carbons is strongly evidenced, although phenyl groups similarly placed tend to retard the reaction.[45] Böeseken[46] also reports that the rates of oxidation of double-bonded carbons in the presence of peracetic acid is greater than that of triple-bonded carbon. The triple bond appears to oxidize by way of the 1,2-diketone and the corresponding dicarboxylic acid. Some investigations conducted by Medvedev and Blokh[47] indicated that the peracid oxidation of cyclohexene is strongly influenced by the solvent used, although the rate depends more on the concentration of peracid than on the concentration of the olefin.

On the other hand, Guillemonat[48] reports that 2-ethylcyclohexene-2 may be oxidized by selenium dioxide in two steps without breaking the double bond. The hydrocarbon was oxidized by selenium dioxide in solution in acetic acid containing some acetic anhydride to yield 37 per cent of 2-ethylcyclohexene-2-acetate. Hydrolysis of this acetate yielded the unsaturated alcohol, 2-ethylcyclohexene-2-ol-1, and the double bond was still unbroken after a second oxidation which converted this compound to the corresponding unsaturated ketone. Similar oxidation of 2-methyl-2-butene yielded 2-methyl-2-butene-1-acetate which could be hydrolyzed to the unsaturated alcohol with the double bond still intact. Hydrogenation (by means of a platinum oxide catalyst) of this alcohol gave the saturated 2-methyl-1-butanol. Similarly, both 2-methylpentene-2 and 3-methylpentene-2 were oxidized to unsaturated alcohols, 2-methylpent-2-en-4-ol and 3-methylpent-2-en-4-ol.

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[43] J. Stuurman, *Proc. Acad. Sci. Amsterdam*, 1935, **38**, 450; *Chem. Abs.*, 1935, **29**, 4657; *Brit. Chem. Abs.* **A**, 1935, 828.

[44] J. Böeseken, van Asperen, C. Auchy, C. Maters and P. Ottenhoff, *Rec. trav. chim.*, 1935, **54**, 657; *Brit. Chem. Abs.* **A**, 1935, 1103; *Chem. Abs.*, 1936, **30**, 3771.

[45] J. Böeseken and J. Stuurman, *Proc. Acad. Sci. Amsterdam*, 1936, **39**, 2; *Chem. Abs.*, 1936, **30**, 3304.

[46] J. Böeseken, *Chem. Weekblad*, 1934, **31**, 166; *Brit. Chem. Abs.* **A**, 1934, 507; *Chem. Abs.*, 1934, **28**, 3395.

[47] S. Medvedev and O. Blokh, *J. Phys. Chem.* (*U.S.S.R.*), 1933, **4**, 721; *Chem. Abs.*, 1935, **29**, 6492; *Brit. Chem. Abs.* **A**, 1936, 939.

[48] A. Guillemonat, *Compt. rend.*, 1935, **200**, 1416; *Brit. Chem. Abs.* **A**, 1935, 852; *Chem. Abs.*, 1935, **29**, 5085. *Compt. rend.*, 1935, **201**, 904; *Brit. Chem. Abs.* **A**, 1936, 51; *Chem. Abs.*, 1936, **30**, 1357.

Ozonolysis of Olefins

Although some oxidants are capable of selectively oxidizing olefin molecules at points other than the double bond, the action of ozone is said to be directed toward the unsaturated linkages. Church, Whitmore and McGrew,[49] in studying the dehydration of alcohols to produce olefins, used this reaction to trace the mechanism involved. Thus, dehydration of methylethylbutyl carbinol yields 55 per cent of 3-methylheptene-2, 30 per cent of 3-methylheptene-3, and 15 per cent of 2-ethylhexene-1, as indicated by the fact that the dehydration products, when ozonized, yielded proportions of the ketones which would be predicted from these unsaturates. The tendency of ozone to split the molecule at the double bond through the intermediate formation of an ozonide can be used in the determination of terminal $H_2C{=}CH$-linkages, according to Doeuvre.[50] A very dilute solution of the olefin to be tested is prepared, using ethyl acetate-acetic acid as the solvent, and the solution treated with ozone at -15 to $-20°C$. The ozonide is then reduced by sulphur dioxide and the formaldehyde which results is determined. Unsaturated compounds containing no terminal methylene groupings give only negligible amounts of formaldehyde. Similarly Clemo and Macdonald[51] report that although the decomposition of an ozonide of a molecule containing a vinyl grouping does yield formaldehyde, the reaction is not unique. Molecules which do not contain this structure may form ozonides which decompose to yield formaldehyde. However, where the vinyl group is present, some 10 times as much formaldehyde is formed. Hence, quantitative estimation of the aldehyde produced affords evidence for the presence of a vinyl residue, although qualitative estimation does not.

Pummerer[52] reports following the ozonolysis of unsaturated compounds by titrating the mixture at intervals with bromine. Thus, 3-ethylpentene-2 was dissolved in carbon tetrachloride, and bromine titrations made at short intervals showed that the olefin was saturated after 10 minutes' treatment with ozone in the apparatus used. In ozonizing cyclohexene under similar conditions, ozone treatment continued for 60 minutes before the bromine titration figures showed saturation. Mesityl oxide, on the other hand, required 45 minutes' operation before the bromine values showed any decline. This was believed to be due to the formation of a primary ozonide less saturated than the final product. When working with rubber and gutta percha solutions, the unsaturation, instead of decreasing, increased during the early part of the ozonolysis until a critical point was reached when the unsaturation values fell suddenly to zero. This fluctuation of values is, similarly, believed due to the formation of primary ozonides. It is suggested, too, that these primary ozonides are the sensitive, explosive substances formed during ozonization. Komppa[53] treated propenylbenzoic acid with ozone for 10 hours till bromine titration values indicated saturation. The ozonide thus formed was an unstable, partially crystalline compound melting at about 180°C. On standing, decomposition took place yielding 83 per cent of *p*-acetobenzoic acid.

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[49] J. M. Church, F. C. Whitmore and R. V. McGrew, *J.A.C.S.*, 1934, **56**, 176; *Chem. Abs.*, 1934, **28**, 1657; *Brit. Chem. Abs.*, **A**, 1934, 276.

[50] J. Doeuvre, *Bull. soc. chim.*, 1936, **3**, 612; *Brit Chem. Abs.* **A**, 1936, 587; *Chem. Abs.*, 1936, **30**, 2917.

[51] G. R. Clemo and J. Mc L. Macdonald, *J.C.S.*, **1935**, 1294; *Chem. Abs.*, 1935, **29**, 7939; *Brit. Chem. Abs.* **A**, 1935, 1390.

[52] R. Pummerer, *IX Congr. intern. quim. pura aplicada*, 1934, **4**, 548; *Chem. Abs.*, 1936, **30**, 2911.

Biphenyl does not form a hexaozonide, but Noller and Kaneko,[54] investigating this problem, have prepared 1-phenyl-1-cyclohexene and report that this compound readily adds 1 mole of ozone to the double bond of the cyclohexene ring. Furthermore, the 1,1′-dicyclohexene adds ozone to both double bonds. These investigators concluded that steric hindrance in the 1-1′ position is not the factor which prevents the formation of biphenyl ozonide. Noller, Carson, Martin and Hawkins[55] studied the ozone absorption rates of a number of compounds and report that oleic acid, methyl oleate and stilbene show rapid addition of 1 molecule of ozone to the double bond. The rate decreases considerably for triphenyl ethylene and compounds containing the grouping $-CH{=}CH-CO-$ (such as crotonic or cinnamic acid). Vinylacetic acid ($CH_2{=}CH-CH_2-CO-OH$) which has a similar, though slightly altered, grouping, shows an analogous, though lessened, retarding effect. A still further decrease was found with tetraphenylethylene and dichloroethylene. In compounds containing two or more double linkages (*e.g.*, diphenylbutadiene, sorbic and elaeostearic acids) rapid addition of one molecule of ozone takes place, but the rate then decreases sharply. In geometrical isomerides which undergo relatively slow addition, such as methyl fumarate and maleate, the *trans* form (the fumaric compound) reacts more rapidly.

OXIDATION OF ALKYNES[56]

According to Lenher and Kistiakowsky,[57] temperatures up to the explosion temperature may be used in the uncatalyzed oxidation of acetylene. These investigators report that formaldehyde, formic acid and glyoxal may be recovered from the reaction products obtained by passing acetylene and oxygen through a reaction tube at from 200°C. to the explosion temperature, though they recommend the range 275 to 316°C. as most desirable.

Steacie and McDonald[58] have investigated the uncatalyzed reaction of acetylene and oxygen and report that the rate of reaction is variable and dependent on the condition of the surface of the reaction vessel. It was found also that the order of the reaction is decreased in a packed vessel,[59] falling to 1.4. Although the ratio of carbon monoxide to carbon dioxide in the reaction products is, in the empty vessel, independent of pressure, in the packed vessel it is at the outset lower than in the empty chamber and falls even further with diminishing pressure. Addition of glyoxal has no appreciable effect on the rate of reaction; formaldehyde, however, decreases it. It was concluded that the oxidation was a chain reaction, the chains being initiated at the walls of the vessel but not destroyed there. The following mechanism was proposed:

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[53] G. Komppa, *Ann. Acad. Sci. Fennicae*, 1935, **44A**, No. 9, 6; *Chem. Abs.*, 1936, **30**, 2945.

[54] C. R. Noller and G. K. Kaneko, *J.A.C.S.*, 1935, **57**, 2442; *Chem. Abs.*, 1936, **30**, 1778; *Brit. Chem. Abs.* **A**, 1936, 321.

[55] C. R. Noller, J. F. Carson, H. Martin and K. S. Hawkins, *J.A.C.S.*, 1936, **58**, 24; *Chem. Abs.*, 1936, **30**, 1739; *Brit. Chem. Abs.* **A**, 1936, 313.

[56] "Triple-bonded hydrocarbons will bear the generic name alkynes." A. M. Patterson, *J.A.C.S.*, 1933, **55**, 3905; *Chem. Abs.*, 1933, **27**, 5304.

[57] S. Lenher and G. B. Kistiakowsky, U. S. P. 1,955,885, April 24, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 182; *Chem. Abs.*, 1934, **28**, 4072.

[58] E. W. R. Steacie and R. D. McDonald, *J. Chem. Physics*, 1936, **4**, 75; *Brit. Chem. Abs.* **A**, 1936, 294; *Chem. Abs.*, 1936, **30**, 1642.

[59] This indicates that the velocity constant is less than that for a second order, but greater than that for a first order reaction. For a discussion of orders of reactions, see Chapter 20.

$$C_2H_2 \xrightarrow{O_2} (C_2H_2O_2) \rightarrow CHO{-}CHO \xrightarrow{O_2} CHO{-}COOOH$$

$$CHO{-}COOOH \left\langle \begin{array}{l} \xrightarrow{(+CHO-CHO)} CHO{-}COOH \rightarrow HCHO + CO_2 \\ \xrightarrow{(+HCHO)} HCOOH \rightarrow CO + H_2O \end{array} \right.$$

According to Lenher,[60] the oxidation of acetylene is catalyzed by the presence of a small quantity of nitric oxides. The presence of this catalyst (4 or 5 per cent) allows the reaction to take place at a considerable rate at a lower temperature. For example, if acetylene (in slight excess) is mixed with oxygen, and 4 to 5 per cent of water vapor and 4 to 5 per cent of nitric oxide added, the reaction takes place at a temperature as low as 170°C. However, 230°C. is recommended, since under these conditions a yield of 21 to 23 per cent of glyoxal is obtained with a contact time of 2 minutes. On the other hand, Heckel and Nashan[61] report that a mixture of acetylene, air and nitric oxides can be reacted at 300°C. to yield acetaldehyde and acetic acid.

Young, Vogt and Nieuwland[62] studied the reactions of the alkyne peroxides and report that the oxidizing properties of these peroxides are in all respects similar to those ascribed to the olefin peroxides. Studies of butylacetylene and analogous compounds showed that the dialkylacetylene forms compounds of a peroxide nature as readily as a monoalkylacetylene. Butylacetylene that had been exposed to the air for about six months gave a good aldehyde test with Schiff's reagent and had a pronounced acid reaction. When a small amount of butylacetylene was allowed to evaporate at room temperature, the residue had a strong odor of valeric acid, although the amount of acid formed was too small to allow of chemical isolation. However, when the alkyne was maintained at 35 to 45°C. for three months, it was found that the peroxide concentration increased rapidly during the first three weeks and remained constant thereafter, while the concentration of valeric acid, on the other hand, increased steadily throughout the experiment. The results were believed to indicate that after a few weeks the rate of formation of the peroxide was approximately equal to the rate at which it oxidized the alkyne, the peroxide being destroyed in the latter step. At the end of the three-month period of heating, titration with standard potassium hydroxide and phenolphthalein showed an acid concentration 2.12 normal. In the meantime, the color of the butylacetylene had progressively changed from water-white to reddish brown.

In an effort to isolate the peroxide, a quantity of the oxidized butylacetylene was distilled through an efficient column. When most of the butylacetylene had been removed, the residue suddenly began to fume and darken, with the evolution of considerable heat. After a few minutes the reaction subsided, leaving a viscous, dark brown and strongly lachrymatory acidic residue. The peroxide appears to be highly unstable when in concentrated form.

It has been suggested that alkynes behave as do the alkenes[63] in oxidation, i.e., that two OH groups first add at the unsaturated bond. Krestinskii and Kelbovskaya[64] attempted to derive some experimental proof of this possible reaction which, with acetylene, should yield the glycol, HOHC=CHOH, at once hydrated to $HOCH_2$-$CH(OH)_2$, and the latter in turn can yield oxalic acid, acetic acid and similar compounds. Acetylene, phenylacetylene, methylethylacetylene and 2,2-dimethylbutyne-3 were studied. Special attention was given to the isolation of any neutral products, and the oxidizing agent (in this case potassium permanganate) was added in very dilute solution at 0°C. to an excess of the hydrocarbon. However, no neutral reaction products could be detected; only acids appeared, cleavage occurring at the triple bond. Acetylene gave formic acid and presumably traces of oxalic. Methylethylacetylene yielded acetic and propionic acids, phenylacetylene gave carbon dioxide, benzoic acid and traces of formic. The 2,2-dimethylbutyne-3 formed 3,3-dimethylbutyric acid.

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[60] S. Lenher, U. S. P. 1,988,455, Jan. 22, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1936, 54; *Chem. Abs.*, 1935, **29**, 1439.

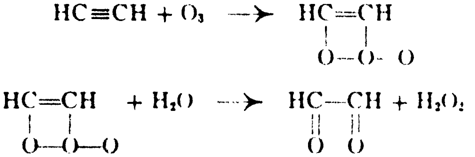
[61] W. Heckel and P. Nashan, U. S. P. 1,943,385, Jan. 16, 1934, to Gutehoffnungshütte Oberhausen A.-G.; *Chem. Abs.*, 1934, **28**, 2018.

[62] C. A. Young, R. R. Vogt and J. A. Nieuwland, *J.A.C.S.*, 1934, **56**, 1822; *Brit. Chem. Abs.* **A**, 1934, 1089; *Chem. Abs.*, 1934, **28**, 6102.

[63] "Open-chain unsaturated hydrocarbons—will bear the generic name alkenes." A. M. Patterson, *J.A.C.S.*, 1933, **55**, 3905; *Chem. Abs.*, 1933, **27**, 5304.

[64] V. N. Krestinskii and M. K. Kelbovskaya, *Ber.*, 1935, **68**, 512; *Brit. Chem. Abs.* **B**, 1935, 604; *Chem. Abs.*, 1935, **29**, 3649.

Acetylene itself reacts with ozone to produce formic acid and glyoxal, but according to Hurd and Christ[65] this is an almost unique case in that most of the alkynes are split at the triple bond by ozonization. However, the reaction has been used to prove the location of the triple bonds in 6,10-hexadecadiyne and in 6,9-pentadecadiyne. Caproic and succinic acids were formed from the latter substance; caproic and malonic from the former. Hurd and Christ investigated the ozonolysis of six acetylene representatives, phenylpropiolic acid, phenylacetylene, 1-hexyne, 1-heptyne, ethinylcyclohexanol and ethinylfenchyl alcohol. In each case, splitting occurred at the triple bond yielding from 42 to 61 per cent of the acids. In the case of 1-heptyne, accurate determinations of both acids showed that two acids (formic and caproic) had been formed in equal quantities, totaling 59.2 per cent. However, despite the fact that a large excess of ozone was employed, no further production of acids took place. These investigators favor the following mechanism in the ozonization and subsequent hydrolysis of acetylene:



$$HC\equiv CH + O_3 \longrightarrow \begin{array}{c} HC{=}CH \\ |\quad\;| \\ O{-}O{-}O \end{array}$$

$$\begin{array}{c} HC{=}CH \\ |\quad\;| \\ O{-}O{-}O \end{array} + H_2O \longrightarrow \begin{array}{c} HC{-}CH \\ \|\quad\;\| \\ O\quad\;O \end{array} + H_2O_2$$

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[65] C. D. Hurd and R. E. Christ, *J. Org. Chem.*, 1936, **1**, 141; *Chem. Abs.*, 1936, **30**, 7108.

Chapter 40

Autoxidation of Petroleum Distillates. Gum Formation

The phenomenon of autoxidation has attracted the interest of many workers It has been defined as the combination of a whole molecule of oxygen with an oxidizable substance to give a primary peroxide which may then change in a number of ways to yield stable oxidation products.[1] This means that 1 molecule of an autoxidizable substance (A) reacts with a molecule of oxygen to furnish the peroxide AO_2. Such peroxides are formed with the absorption of energy and may then decompose to yield various products or react with other molecules of the autoxidizable substance.

Many substances may undergo autoxidation, among them being phosphorus and sulphur compounds, sodium bisulphite, benzaldehyde, paraffin, petroleum distillates, rubber and turpentine.[1a] Catalysts may also play a very large part in such phenomena. Thus, Suzuki[2] showed that oxides and some salts of lead, cobalt and manganese exert a stronger effect on the oxidation of *d*-α-pinene than do the oxides of platinum, silver, chromium or thallium. Furthermore, the oleates of lead, cobalt and manganese are more active catalytically than the corresponding stearates or sulphates. Temperature is also an important factor in many instances. For example, above 40°C. oxidation of pinene yields verbenone and verbenol and polymerized substance, whereas below 20°C. the product is a viscous mass consisting mainly of the peroxide.

AUTOXIDATION OF HYDROCARBONS

Among autoxidizable substances which lend themselves to study, tetralin (tetrahydronaphthalene) has received considerable attention because of the ease with which its peroxide may be isolated.[3] The latter may be obtained by extracting aged tetralin (i.e., a sample which has been stored in contact with air) with caustic soda,[4] or by bubbling air through tetralin heated to 75°C. and removing the unreacted hydrocarbon by distillation at reduced pressures.[5] Since the study of tetralin peroxide gives some insight into the nature of the intermediate products of autoxidation, it is of interest to discuss some of its properties.

Tetralin peroxide melts at 56°C. It is stable for a short time at 120 to 125°C. and loses water at 130°C. Above this latter temperature it explodes. Treated with potassium permanganate it furnishes β-*o*-carboxyphenyl propionic acid:

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[1] C. Moureu, C. Dufraisse and R. Chaux, *Compt. rend.*, 1927, **184**, 413; *Chem. Abs*, 1927, **21**, 1914; *Brit. Chem. Abs.* **B**, 1927, 243.

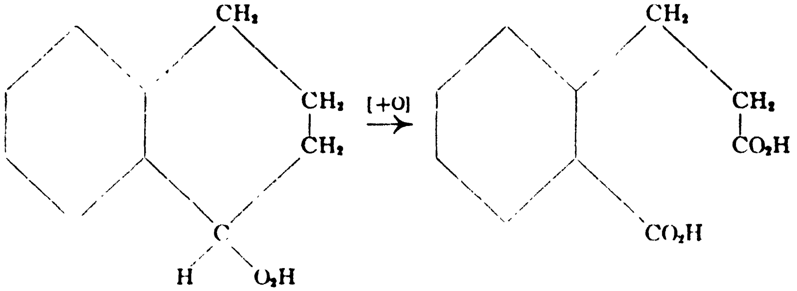
[1a] For a discussion of the effect of repressuring crude petroleum with air and gas, see T. W. Johnson and S. S. Taylor, *Bur. Mines Rept of Investigations* **3325**, 1937; *Chem. Abs.*, 1937, **31**, 2802. S. S. Taylor and H. M. Smith, *Bur. Mines Rept. of Investigations* **3238**, 1934; *Chem. Abs.*, 1934, **28**, 4579.

[2] K. Suzuki, *Bull. Inst. Phys.-Chem. Research (Tokyo)*, 1935, **14**, 179; *Chem. Abs.*, 1935, **29**, 5830.

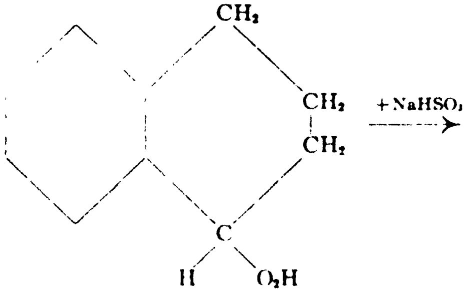
[3] Decalin forms a peroxide much less readily than tetralin. T. Yamada, *J. Soc. Chem. Ind., Japan*, 1936, **39**, Suppl. binding 20; *Chem. Abs.*, 1936, **30**, 4305; *Brit. Chem. Abs.* **B**, 1936, 355.

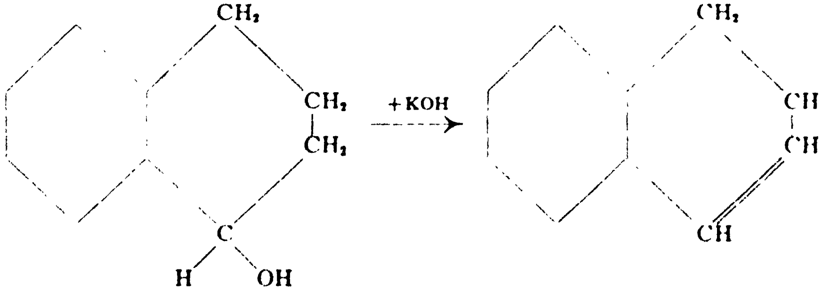
[4] H. Kiemstedt, *Brennstoff-Chem.*, 1936, 17 (5), 83; *Brit. Chem. Abs.* **B**, 1936, 484.

[5] H. Hock and W. Susemihl, *Ber.*, 1933, **66**, 61; *Brit. Chem. Abs.* **A**, 1933, 153; *Chem. Abs.*, 1933, **27**, 1627.



The peroxide is reduced by potassium iodide in aqueous acetic acid, or better by sodium bisulphite in aqueous methanol, to give tetrahydro-α-naphthol. The latter loses water when treated with freshly melted potassium hydroxide and forms 1-2-dihydronaphthalene. Warm caustic soda solution (*2N*) converts the peroxide into 1-ketotetrahydronaphthalene.





Tetralin peroxide reacts with iron carbonyl to give a dark red coloration and liberate gas.[6] It darkens mercury and prevents sulphur in liquid fuels from discoloring copper, according to Kiemstedt.[7]

The formation of tetralin peroxide is not affected by light or contact substances.[8] Tanaka, Kuwata and Aoki[9] studied the effect of phenols and naphthols on the autoxidation of tetralin and found the inhibiting power of phenol was decreased by the introduction of methyl, nitro or chloro groups. Polyhydroxybenzenes and naphthols, however, were powerful inhibitors. Amines were less effective than the corresponding hydroxy compounds, and alcohols, aldehydes, ketones and acids showed no effective inhibition.

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[6] H. Hock and W. Susemihl, *Brennstoff-Chem.*, 1933, 14, 106; *Brit. Chem. Abs.* B, 1933, 421; *Chem. Abs.*, 1933, 27, 3803.

[7] H. Kiemstedt, *loc. cit.*

[8] H. Hock and W. Susemihl, *loc. cit.*

[9] Y. Tanaka, T. Kuwata and M. Aoki, *J. Soc. Chem. Ind. (Japan)*, Suppl. binding; 1934, 37, 445; *Brit. Chem. Abs.* B, 1935, 12; *Chem. Abs.*, 1934, 28, 7253; *J. Inst. Pet. Tech.*, 1934, 20, 609A.

Decalin (decahydronaphthalene) forms autoxidation products more slowly than tetralin.[10] Castiglioni[11] reports that light, especially ultraviolet, accelerates this reaction. By noting changes in acidity, the degree of oxidation may be determined[12] for a particular set of conditions. However, the addition of 0.001 to 0.01 per cent of pyrogallol, hydroquinone or α-naphthol is said to retard the autoxidation of decalin very markedly.[13] Other hydrocarbons found to undergo autoxidation are unsaturated cyclic compounds as 1-methyl-1-cyclohexene and 1-methyl-3-cyclohexene.[14]

Catalysis of Autoxidation Reactions

Arditti[15] noted that there is an induction period in the absorption of oxygen by normal hexadecane which is decreased by higher temperatures. The rate of absorption increased rapidly after the initial induction period and then diminished nearly to zero. The first product of oxidation by the absorbed oxygen was carbon monoxide, while later the dioxide was also formed. An amount of hydrogen and methane proportional to the oxygen absorbed was formed. This same investigator[16] studied the effects of several substances on the oxidation of paraffin oil by oxygen bubbled through it at 130°C. and found that copper, nickel, nickel oxide and cupric oxide catalyzed the reaction, whereas aniline, *n*-hexadecane, ferric oxide, phenol and water inhibited it. Dupont[17] determined the catalytic effects of acetylacetone and various metallic acetylacetonates on the autoxidation of 1,4-dimethylcyclohexane and phenylcyclopentane. He reported that the order of decreasing activity of metal-acetylacetone complexes in either case was cobalt(ous and ic), copper, manganese, iron and cerium. In the experiments on phenylcyclopentane allowance was made for the fact that this substance absorbs oxygen spontaneously. Dupont believed that the oxidation of these hydrocarbons was autocatalytic to a certain extent, but that catalysis also played a part.

Stephens[18] noted that autocatalysis played an insignificant part in the autoxidation of cyclohexene at 28°C. The hydrocarbon was purified rigorously and it was shown that the induction period decreased with increasing purity, but did not disappear even with the most highly purified material. Arsenic trioxide, which is occasionally present in glassware, was an inhibitor. He concluded that the induction period was caused by inhibitors present in minute amounts.

Gum in Gasoline

The autoxidation of gasoline has been the object of extended study by many investigators[19] because of its formation of gum, the latter being a deleterious com-

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[10] C. Moureu, C. Dufraisse and R. Chaux, *Compt. rend.*, 1927, **184**, 413; *Chem. Abs.*, 1927, **21**, 1914; *Brit. Chem. Abs* **B**, 1927, 243.

[11] A Castiglioni, *Gazz. chim. ital.*, 1934, **64**, 465; *Chem. Abs.*, 1935, **29**, 30; *Brit. Chem. Abs.* **A**, 1934, 1184.

[12] P. Panyutin, L. Hindin and O. Vasil'eva (*Compt. rend. acad. sci U.R.S.S.* (*N.S.*), 1936, **2**, 183; *Chem. Abs.*, 1936, **30**, 8073) describe a laboratory procedure for determining the peroxide number of an unsaturated hydrocarbon that has undergone autoxidation.

[13] A. Castiglioni, *Ann. chim. applicata*, 1936, **26**, 106; *Chem. Abs.*, 1936, **30**, 6631.

[14] R. Dupont, *Bull. soc. chim. Belg.*, 1936, **45**, 57; *Brit. Chem. Abs.* **A**, 1936, 712; *Chem. Abs.*, 1936, **30**, 7549.

[15] G. Arditti, *Compt. rend.*, 1935, **201**, 396; *Chem. Abs.*, 1935, **29**, 7269.

[16] G. Arditti, *Compt. rend.*, 1932, **195**, 136; *Chem. Abs.*, 1932, **26**, 5062; *Brit. Chem. Abs.* **B**, 1933, 137.

[17] R. Dupont, *Bull. soc. chim. Belg.*, 1936, **45**, 113; *Chem. Abs.*, 1936, **30**, 4746.

[18] H. N. Stephens, *J.A.C.S.*, 1936, **58**, 219; *J. Inst. Pet. Tech.*, 1936, **22**, 204A; *Chem. Abs.*, 1936, **30**, 2476; *Brit. Chem. Abs.* **A**, 1936, 434.

[19] See Carleton Ellis "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., New York, 1934. Also J. C. Morrell and G. Egloff, *Nat. Pet. News*, 1936, **28** (13), 24-G; *Chem. Abs.*, 1936, **30**, 4656. L. v. Szeszich, *Brennstoff-Chem.*, 1934, **15**, 421; *Chem. Abs.*, 1935, **29**, 1960; *Brit. Chem. Abs.* **B**, 1935, 54. A review of gum in gasoline is given by E. B. Evans, *J. Inst. Pet. Tech.*, 1934, **20**, 392-408A; *Chem. Abs.*, 1934, **28**, 4581.

TABLE 184.—

	Carbon %	Hydrogen %	Sulphur %	Oxygen %	Mol. Weight
Oxidized[a]					
Entire oxidized gasoline	84.4	13.4	0.03	2.2	
Light distillate	85.4	14.7	0.02	2.2	
Heavy distillate	86.4	13.5	0.02	0.1	
Residue	69.6	9.2	0.42	20.8	342
Stored[b]					
Entire oxidized gasoline	85.1	13.9	0.06	0.9	
Light distillate	86.1	14.0	0.02	0	
Heavy distillate	86.5	13.5	0.02	0	346
Residue	69.8	8.7	0.40	21.1	

[a] Oxidized by oxygen under pressure until a 20 pounds per sq. in. (1.4 kg. per sq. cm.) pressure drop occurred.
[b] For gasoline used in elementary analysis the time was not specified. It was 86 days for the other samples.

ponent when present in sufficient proportions in motor fuels.[20] Of the unsaturated hydrocarbons present in cracked distillates, diolefins are particularly prone to gum formation.[21] The oxidation-polymerization of unstable constituents of the gasoline is thought to form gasoline-soluble colloids which coagulate and become gasoline-insoluble. This statement is supported by the respective compositions of gasoline-soluble and -insoluble gums which average about 70 per cent carbon, 7 per cent hydrogen, 21 per cent oxygen and 2 per cent sulphur and ash in each case.

The gum remaining after the evaporation of oxidized, cracked gasoline was studied by Morrell and co-workers.[22] They oxidized the gasoline in steel bombs[23] at an initial pressure of 135 pounds and a temperature of 100°C. Oxidation was stopped 10 minutes before the beginning of the rapid oxygen absorption and after the pressure had dropped 5, 10, 20 and 50 pounds by running cold water around the bomb. Analysis was made of the gasoline from each experiment by concentrating it by evaporation under about 2 mm. pressure at 79°C. The vapors were condensed by passage through an ice-bath and afterwards by an acetone and carbon dioxide mixture. This gave three fractions, i.e., a residue and two condensates, each of which was studied. These investigators found that the residue contained peroxides, aldehydes and acids and that these products were present in practically the same proportion regardless of the state of oxidation.

The products formed by oxidation under pressure and at slightly elevated temperatures (accelerated oxidation) differed somewhat in the specific compounds present from those formed during storage, but only slightly in elementary composition as is shown by some of the data of Morrell and co-workers in Table 184.

In the former case, peroxides and acids were present in the greatest amount in the residue and light fractions, respectively, whereas all oxygen-containing products were present in greatest amount in the residue from stored gasoline. Oxidation was accelerated by evaporation in a copper dish, and on reaching dryness peroxides were largely decomposed. These investigators concluded that peroxides represent the first step in gum formation and are essential to it, although acids and aldehydes may have some significance since the insoluble mass

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[20] The carbon deposit on the inlet valves of experimental engines run on cracked gasoline containing from 2.4 to 31.6 mg. of dissolved gum caused no trouble, although it might on prolonged running. B. K. Tarasov and V. P. Govakov, *Groznenskii Neftyanik*, 1934, 4 (23), 76; *Chem. Abs.*, 1935, **29**, 2724; *Brit. Chem. Abs.* **B**, 1935, 1031.

[21] A. Sakhanov, *Petroleum Z.*, 1934, **30** (25), 1; *Brit. Chem. Abs.* **B**, 1934, 788; *Chem. Abs.*, 1935, **29**, 1236. *Chimie & Industrie*, 1934, **32**, 770; *Chem. Abs.*, 1935, **29**, 1615; *J. Inst. Pet. Tech.*, 1935, **21**, 49A; *Brit. Chem. Abs.* **B**, 1934, 1045. See also J. C. Morrell and G. Egloff, "Colloid Chemistry of Petroleum," in J. Alexander, "Colloid Chemistry," The Chemical Catalog Co., Inc., 1931.

[22] J. C. Morrell, C. G. Dryer, C. D. Lowry, Jr. and G. Egloff, *Ind. Eng. Chem.*, 1936, **28**, 465; *Chem. Abs.*, 1936, **30**, 3990; *J. Inst. Pet. Tech.*, 1936, **22**, 264A.

[23] For the details of the equipment used, see G. Egloff, J. C. Morrell, C. D. Lowry, Jr. and C. G. Dryer, *Ind. Eng. Chem.*, 1932, **24**, 1375.

Analyses for Pennsylvania Cracked Gasoline.

Peroxide Units	Aldehyde Units	Acid Units	Copper-Dish Gum (mg./100 cc.)	A.S.T.M. Gum (mg./100 cc.)	Per Cent of Total Gasoline
9150	1660	375	960	123	100
207	545	204	14	2	54.5
2115	334	81	413	87	40.3
2844	450	198	—	—	1.8
7100	1660	100	983	128	100
132	234	39	3	0	52
1395	225	25	209	12	45
3196	680	51	—	—	1.7

which sometimes precipitated during oxidation has a high acid content. The formation of peracids during the storage of gasoline derived from sapropelite, was shown by Karavaev and Kuruindin.[24] In this instance the stock had been previously treated with sulphuric acid and distilled over sodium.

According to McNamara[25] certain treatments, such as vapor phase refining with zinc chloride, hydrogenation, or blending with straight-run gasoline, increase the induction period whereas doctor-treating and sunlight accelerate oxidation. He also states that a rise in temperature of 20°F. roughly trebles the rate of gum-formation.

Shchitikov[26] found that thorough washing with water considerably improved the color and decreased the potential gum content and acidity of a cracked distillate after preliminary neutralization. He recommended two caustic treatments before redistillation. He also stated that the stability is lower and the gum formation higher when the finished cracked gasoline is treated with sodium hydroxide or sodium carbonate. Gerr and co-workers[27] pointed out that the diolefins which caused the instability of cracked gasoline were removed by refining. They observed that the higher boiling fractions were the more stable, but that all fractions needed refining. The gasoline obtained by treatment of the cracked distillate from Emba crude oil with kerosene acid sludge, followed by neutralization and distillation is reported to be very unstable.[28]

Weller[29] observed that a blended fuel containing 10 per cent alcohol had a 50 per cent shorter induction period than the original fuel, but he did not regard the induction period as conclusive in the determination of stability of fuels to gum formation. Conrad[30] showed that different tests may give widely varying results and fail to indicate the behavior of the fuel when kept for long periods of time. For example, the copper dish and Hunn bomb tests failed to give values which corresponded to gum-formation occurring during storage of the fuel for 10 months. He also demonstrated that the relative amount of gum formed on storage was not a linear function of the time. Gasoline with an induction period of 240 minutes, or potential gum of 50 mg. or less, is reported to be satisfactory in normal storage for periods of less than 1 year.[31]

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[24] N. M. Karavaev and K. S. Kuruindin, *Khim. Tverdogo Topliva*, 1933, 4, 315; *Chem. Abs.*, 1934, **28**, 6281; *Brit. Chem. Abs.* B, 1935, 53.

[25] L. McNamara, *Refiner*, 1934, 13, 381; *J. Inst. Pet. Tech.*, 1935, 21, 17A; *Brit. Chem. Abs.* B, 1935, 1031; *Chem. Abs.*, 1935, **29**, 2720.

[26] V. K. Shchitikov, *Groznenskii Neftyanik*, 1934, 4 (11-12), 56; *Chem. Abs.*, 1936, **30**, 3990.

[27] V. F. Gerr, A. F. Dudenko and K. S. Assman, *Azer. Neft. Khoz.*, 1935, No. 6, 83; *Chem. Abs.*, 1936, **30**, 3990.

[28] N. N. Karskii and V. M. Gluizdenok, *Neft. Khoz.*, 1934, 26 (5), 53; *Chem. Abs.*, 1934, **28**, 7503.

[29] R. Weller, *Oel und Kohle*, 1934, 2, 527; *J. Inst. Pet. Tech.*, 1935, 21, 52A; *Chem. Abs.*, 1936, **30**, 5389.

[30] C. Conrad, *Oel und Kohle*, 1935, 11, 728; *Brit. Chem. Abs.* B, 1935, 1031.

[31] A. W. Trusty, *Refiner*, 1935, 14, 47; *Chem. Abs.*, 1935, **29**, 2720.

DETERMINATION OF GUM

Efforts to ascertain the degree of gum formation in gasoline have resulted in several methods for the estimation of both potential and existent gum.[32] One of the oldest is the well-known copper dish. Since the results obtained by this procedure are not reproducible with accuracy because of the catalytic action of the metal, it has been modified by employing a glass or porcelain dish. The rate of evaporation is frequently increased by directing a jet of air towards the center of the sample.

For determination of the actual gum present in cracked gasoline, Woog, Givaudon and Dacheux[33] suggest evaporation of the sample at slightly elevated temperatures in an apparatus arranged so that steam from a water-bath (the heating medium) cannot come in contact with the test dishes. They give the following details: A Pyrex dish is thoroughly cleaned and dried at 160°C. for 45 minutes. After being cooled at least 2 hours in a desiccator and weighed to 0.1 mg., 100 cc. of gasoline are added and evaporated in the apparatus for 3 hours. Afterwards the dish and any residue are dried in an oven for 6 to 8 hours at 160°C., or if the residue is wet it is first dried at 100°C. for 2 hours and then at the higher temperature. The dish is cooled for at least 2 hours in a desiccator and weighed. Gasoline which contains less than 10 mg. of gum per 100 cc. causes no trouble in an engine.

Engine conditions were simulated by drawing atomized gasoline and air through a horizontal aluminum tube containing an aluminum helicoid. This was maintained at 105 to 110°C. in an electric oven. During the course of 5 hours, the vapors from 1100 cc. of gasoline were drawn through this apparatus by a vacuum of 20 mm. The amount of gum formed by this procedure showed a definite relationship to the "actual" gum as determined by the above evaporation test.

For estimating potential gum, Woog, Givaudon and Dacheux recommend that the sample be exposed to ultraviolet light for 30 to 60 minutes and then heated under pressure with oxygen at 100°C. for 2 to 3 hours. The resulting gum is then determined by evaporation of the treated liquid. Thomas,[34] on the other hand, considers subjecting the sample for 20 minutes to the action of oxygen at 100°C. under 10 pounds pressure as sufficiently vigorous treatment.[35]

Freund[36] developed a method for estimating gum in which the sample was placed in a quartz tube and exposed to the light of a standardized mercury-vapor lamp for 10 minutes at 15 to 25°C. Gum formed by this procedure and by oxidation differed largely in respect to oxygen content. The type of atmosphere in which

TABLE 185.—*Composition of Gum Formed on Oxidation of Gasoline.*

			Composition on Ash-Free Basis				As Pure CH Substance		
Method of Oxidation	Duration of Treatment	Atmosphere in Which Gum Was Dried	C	H	S	O (diff.)	C	H	C/H Ratio
Exposure to ultraviolet light	40 min.	Air oven	80.82	8.57	2.41	8.20	90.4	9.6	9.4
Storage	253 days	" "	74.51	7.77	1.29	16.43	90.6	9.4	9.6
Oxygen bomb test	—	" "	72.61	7.82	1.67	17.90	90.3	9.7	9.3
Exposure	40 min.	Nitrogen	84.51	9.42	0.95	5.12	90.0	10.0	9.0
Storage	354 days	"	6.50	8.57	0.17	14.76	89.9	10.1	8.9

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[32] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[33] P. Woog, J. Givaudon and P. Dacheux, *Rev. pétrolifère*, 1934, 584, 721; *J. Inst. Pet. Tech.*, 1935, 21, 52A; *Chem. Abs.*, 1934, 28, 7501.

[34] W. H. Thomas, *Proc. World Petr. Congr.*, 1933, 2, 122; *J. Inst. Pet. Tech.*, 1934, 20, 83A; *Chem. Abs.*, 1934, 28, 4879; *Brit. Chem. Abs.* B, 1934, 819.

[35] A review of methods of gum determination, both actual and potential, is given by W. H. Hoffert, *Chaleur & ind.*, 1934, 15 (167), 389; *Chem. Abs.*, 1934, 28, 6558.

[36] M. Freund, *Proc. World Petr. Congr.*, 1933, 2, 108; *Brit. Chem. Abs.* B, 1934, 819; *J. Inst. Pet. Tech.*, 1934, 20, 83A; *Chem. Abs.*, 1934, 28, 4879.

the gum was dried also had some influence on the oxygen content. Table 185 shows some of his data for samples of a gasoline derived from a Dubbs-cracked Moreni crude oil.

From this it is evident that the highest oxygen content occurs in gum formed by oxidation in a bomb. When the gum was dried in an atmosphere of nitrogen, the composition showed somewhat less oxygen than if dried in air. However, the relative proportion of carbon and hydrogen in the gum was practically independent of the manner of formation. Mardles and Moss[37] incubated gasoline samples prior to the determination of existent gum by storing them at 35°C. for 20 hours in the dark. The usual sample was 50 cc. in a 500 cc. long-necked, glass-stoppered flask. The gum found (by evaporation in a glass dish) after this treatment corresponded rather closely to that formed after 3 months' storage, as is shown in Table 186.

TABLE 186. - *Comparison between Potential Gum Test and Gumming During Storage.*

	Gum Increase in mg. per 100 ml.	
Fuel	At 35°C. for 20 Hours in 1/10 Filled Flask	At 12.5°C. for 3 Months in Nearly Full Tin Containers
Benzol	3	6
Low temp. coal distillate (A)	8	3
Low temp. coal distillate (B)	3	5
Cracked distillate	40	20
Vapor phase cracked distillate	55	65
Hydrogenated coal distillate	1	1

These investigators suggested that the test may be accelerated still further by increasing the temperature to 50° or 75°C.

Treatment of 20 cc. of gasoline in a Dewar flask with a 20 per cent solution of stannic chloride and measuring the rise in temperature was suggested by Kogerman[38] as a procedure for determining the instability of a motor fuel. This method, however, is not applicable to fuels containing alcohols.

The standard methods of the American Society for Testing Materials[39] and the Institute of Petroleum Technologists[40] depend upon a current of air blowing across the sample while evaporation is taking place. The comparison of these tests given in Table 187 is of interest.

Bridgeman[41] found that by using a sufficient air flow over the gasoline sample during determination of gum by the usual methods, the other factors which often affect the results, such as the volume of gasoline evaporated, the concentration of gum-forming constituents and the temperature of evaporation, had very little effect. The same values for gum were obtained whether the air flow was 320 or 680 ml. per second.

A rapid titrometric method for the estimation of gum has been proposed[42] which comprises distillation of the sample and titration of the residue. The recommended procedure is: Distil 100 cc. of the sample in an Engler flask on an oil bath at 160°C., at atmospheric pressure, for 15 minutes and then under vacuum which

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[37] E. W. J. Mardles and H. Moss, *Proc. World Petr. Congr.*, 1933, **2**, 116; *Chem. Abs.*, 1934, **28**, 4879; *J. Inst. Pet. Tech.*, 1934, **20**, 169A; *Brit. Chem. Abs.* **B**, 1934, 819.

[38] P. N. Kogerman, *Proc. World Petr. Congr.*, 1933, **2**, 113; *Brit. Chem. Abs.* **B**, 1934, 819; *Chem. Abs.*, 1934, **28**, 4879; *J. Inst. Pet. Tech.*, 1934, **20**, 311A.

[39] Tentative method of test (D 381-34T) for gum content of gasoline, American Society for Testing Materials, Philadelphia, 1934.

[40] Standardization Sub-Committee on Gum, Institute of Petroleum Technologists, *Proc. World Petr. Congr.*, 1933, **2**, 94; *Brit. Chem. Abs.* **B**, 1934, 1045; *Chem. Abs.*, 1934, **28**, 4879; *J. Inst. Pet. Tech.*, 1934, **20**, 83A.

[41] O. C. Bridgeman, *Proc. World Petr. Congr.*, 1933, **2**, 97; *J. Inst. Pet. Tech.*, 1934, **20**, 309A; *Chem. Abs.*, 1934, **28**, 4879; *Brit. Chem. Abs.* **B**, 1934, 1045.

[42] P. Woog, J. Givaudon and A. Chmelewsky, *Rev. pétrolifère*, 1935, **635**, 757; *Chem. Abs.*, 1935, **29**, 6035; *J. Inst. Pet. Tech.*, 1935, **21**, 374A.

TABLE 187.—*Comparison of Standard Tests for Gum.*

	ASTM Specifications	IPT Specifications
Sample container	Beaker, one size only (100 ml.)	Hemispherical dish Size a-25 cc. sample (6 cm. dia., 3 cm. height) Size b-50 cc. sample (9 cm. dia., 5 cm. height)
Heating medium	Closed bath of 3 per cent water in ethylene glycol	Open steam bath
Temperature of evaporation	160-165.8°C.	100°C.
Flow of air	One liter per second over the entire surface	Jet impinging at one point. For 25 cc. sample air pressure equivalent to 1 cm. of water. For 50 cc. sample air pressure equivalent to 2 cm. of water.
Temperature of the air	Preheated to 151.7-160°C.	Cold
Quantity for test	50 cc.	25 or 50 cc. depending on gum content
Time for evaporation	About 30 min.	60 min. or more

is so regulated that the distillation is resumed at the rate of 2 drops a second. After 5 minutes the vacuum should reach 30 to 50 mm. of mercury and should be so maintained until the end of this operation. The residual gum is dried by continued heating (under reduced pressure). The total time for distillation and drying should be 40 minutes. After cooling and blowing oil from the neck of the flask, the gum is dissolved in 15 cc. of carbon tetrachloride and titrated in the following manner. To the solution are added 15 cc. of 20 per cent sulphuric acid and 20 cc. of 0.1*N* potassium permanganate, all of which is then heated over a direct flame and agitated for 3 minutes after the solvent starts to boil. Then 2 cc. of a solution of 25 g. potassium iodide in 100 cc. of water, 10 cc. of 0.1*N* sodium thiosulphate solution and 1 cc. of starch solution are added and the excess potassium permanganate determined. One milligram of gum is equivalent to 1 cc. of 0.1*N* potassium permanganate.

Egloff and co-workers[43] have investigated and discussed various procedures for determination of gum content and concluded that none is wholly satisfactory. They state that the air-jet method gave some correlation between experimental results and gum deposition in motor cars. Further that the copper-dish test was of value in predicting storage stability, particularly if considered in conjunction with the oxygen bomb test.[44]

INHIBITION OF GUM FORMATION

Because the addition of antioxidants increases the induction period in gum formation, and because it protects the gasoline for some time from various oxidative changes, many workers have advocated the use of oxidation inhibitors in gasolines.[45] It is well known that cracked distillates give gasolines which are superior in many performance characteristics to the analogous straight-run fractions when used similarly.[46] The presence in these cracked motor fuels of many conjugated and other diolefins makes them susceptible to oxidation and the formation of gums. However, incorporation of inhibitors ameliorates these tendencies to a considerable extent. Rogers and Voorhees[47] observed that the solubility of an inhibitor should be less in water than in gasoline. Many useful inhibitors, such as catechol, hydroquinone, pyrogallol and benzyl-*p*-aminophenol are not very soluble in gasoline. Thomas[48] has overcome this difficulty by dissolving them in cresol and adding this solution to the fuel. He found that the above compounds were the most effective of some sixty substances investigated.

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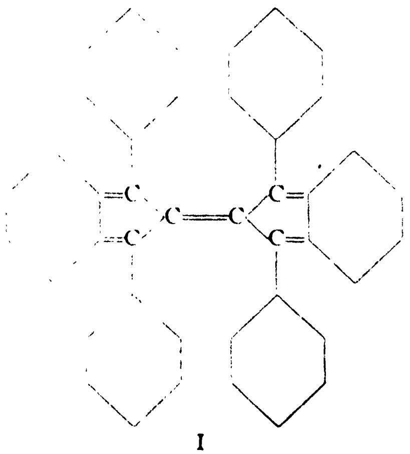
[43] G. Egloff, J. C. Morrell, C. Wirth III and G. B. Murphy, *Proc. World Petr. Congr.*, 1933, **2**, 85; *Brit. Chem. Abs.* **B**, 1934, 819; *J. Inst. Pet. Tech.*, 1934, **20**, 310A; *Chem. Abs.*, 1934, **28**, 4879.

[44] The determination of gums dissolved in kerosene and cracked kerosene distillates are given, respectively, by B. K. Tarasov and V. V. Rudenko (*Groznenskii Neftyanik*, 1934, **4** (1), 65; *Chem. Abs.*, 1935, **29**, 2720; *Brit. Chem. Abs.* **B**, 1935, 1032) and L. A. Aleksandrov (*Groznenskii Neftyanik*, 1934, **4** (1), 66; *Chem. Abs.*, 1935, **29**, 2720; *Brit. Chem. Abs.* **B**, 1935, 1032).

[45] See, for example, *Chem. Trade J.*, 1935, **97**, 25, 49, 69, 115, 133; *J. Inst. Pet. Tech.*, 1935, **21**, 414A. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

Lowry and co-workers[49] reported results obtained by using various dyestuffs as inhibitors of gum formation. Indophenol and leucoindophenol were the best of those tried. In almost all cases azo-dyestuffs were inferior to the phenols from which they were prepared.

These investigators found that it was possible to estimate colorimetrically the extent to which an inhibitor had become exhausted if there was present a dyestuff with inhibiting power. Although not strictly accurate, a rather close approximation was possible on the assumption that both the dyestuff and inhibitor were consumed at the same rate so that their relative amount would always be constant. As an example, they reported an experiment in which phenylazo-α-naphthol and α-naphthol were used; the results are shown in Table 188. Although the figures do not check very closely, they are in sufficient agreement to be of some interest. Another example of a colored substance which has been used to follow the course of the depletion of inhibitors is rubrene.[50]



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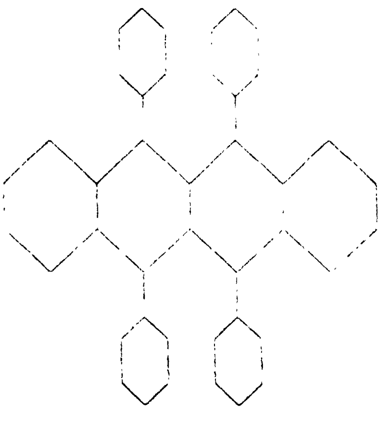

II

rubrene[51]

The influence of various substituent groups on the inhibiting properties of or-

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[46] N. Mayer, *Chem.-Ztg.*, 1935, **59**, 843; *Brit. Chem. Abs.* **B**, 1936, 308. W. H. Hoffert, *Chaleur et ind.*, 1934, **15** (167), 389; *Chem. Abs.*, 1934, **28**, 6558. See also Carleton Ellis, *loc. cit.*

[47] T. H. Rogers and V. Voorhees, *Proc. World Petr. Congr.*, 1933, **2**, 63; *J. Inst. Pet. Tech.*, 1934, **20**, 311A; *Brit. Chem. Abs.* **B**, 1934, 1045. Also, *Oil Gas J.*, 1933, **32** (11), 13, 28; *Chem. Abs.*, 1933, **27**, 5525.

[48] W. H. Thomas, *Proc. World Petr. Congr.*, 1933, **2**, 44; *Brit. Chem. Abs.* **B**, 1934, 1045; *J. Inst. Pet. Tech.*, 1934, **20**, 323A. See also *Refiner*, 1933, **12**, 321; *Chem. Abs.*, 1933, **27**, 5525.

[49] C. D. Lowry, Jr., G. Egloff, J. C. Morrell and C. G. Dryer, *Ind. Eng. Chem.*, 1935, **27**, 413; *Chem. Abs.*, 1935, **29**, 3816; *Brit. Chem. Abs.* **B**, 1935, 614; *J. Inst. Pet. Tech.*, 1935, **21**, 210A. See also *Oil Gas J.*, 1934, **33** (20), 35; *J. Inst. Pet. Tech.*, 1935, **21**, 21A, and Dutch P., 62,270, 1932, to Standard Oil Development Co.; *J. Inst. Pet. Tech.*, 1935, **21**, 175A.

[50] French P. 765,424, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 6995. Rubrene loses its red color (with yellow fluorescence) on oxidation.

[51] Structural formula II is that suggested by E. Bergmann and E. Herlinger, *J. Chem. Physics*, 1936, **4**, 532; *Chem. Abs.*, 1936, **30**, 6361.

TABLE 188.—*Exhaustion Rate of Inhibitors.*

Oxidation Period Min.	Loss of Phenyl-azo-α-Naphthol Per Cent	Consumption of α-Naphthol Determined[a] Per Cent	Consumption of α-Naphthol Calculated Per Cent
100	20	20	28
Over 200	Over 50	Over 60	Over 48

[a] Determination of α-naphthol made by reaction with 2,6-dibromoquinone chlorimide.

ganic substances has been outlined by Lowry[52] and Egloff and co-workers.[53] The presence of an easily oxidizable group, such as aromatic hydroxy or primary or secondary amino groups, or multiples of these, as well as alkyl, aryl or tertiary amino groups, ortho or para to the amino or hydroxy groups, gives increased inhibiting power. The presence of nitro, carbonyl or carboxyl radicals has the opposite effect. Egloff, Morrell, Lowry and Dryer proposed that the antioxidant be added to the gasoline before the latter has been exposed to air. Other methods in which the antioxidants may be added have been suggested.[54] Thus, the cracked gasoline may be treated with acid, redistilled and the antioxidant incorporated. It may be clay-treated before adding the inhibitor, or the inhibitor may be added to a cracked fraction, which is then blended with the main body of the fuel.[55] Mardles[56] found that the inhibiting power of substances varied in different fuels and in different concentrations. Bickmore[57] recommended, therefore, that the specific inhibitor and its optimum concentration be determined for a fuel. Furthermore, he reported that most of the gum-forming substances can usually be found in the fraction boiling between 86° and 116°C. Degtyarèva[58] reported that hydroquinone was the best inhibitor and pyrogallol next best.

Sager[59] has isolated an inhibitor, consisting of *p*-cresol, by acidifying the caustic soda wash from a Rumanian cracked distillate. It was less effective than the commercially available cresol but also much less expensive. Lowry and Dryer[60] inhibited autoxidation by the addition of tars formed during the destructive distillation of wood. The fractions of lignite[61] and coal tar[62] boiling from about 200 to 300°C. have been used for the same purpose. Benedict[63] proposed to add the reaction product from an alkyl amine and wood tar or an aliphatic acid to gasoline.

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[52] C. D. Lowry, Jr., *Trans. Electrochem. Soc.*, 1936, **69**, 279; *Chem. Abs.*, 1936, **30**, 3989; *Brit. Chem. Abs.* **B**, 1936, 581.

[53] G. Egloff, J. C. Morrell, C. D. Lowry, Jr. and C. G. Dryer, *Proc. World Petr. Congr.*, 1933, **2**, 50; *Brit. Chem. Abs.* **B**, 1934, 743; *J. Inst. Pet. Tech.*, 1934, **20**, 254A.

[54] See, for example, *Oil Gas J.*, 1934, **32** (42), 36; *J. Inst. Pet. Tech.*, 1934, **20**, 323A.

[55] The autoxidation of fats may be inhibited by the addition of substances which have found use in petroleum distillates for the same purpose. H. S. Olcott, *J.A.C.S.*, 1934, **56**, 2492; *Brit. Chem. Abs.* **B**, 1935, 68. Autoxidation of hydrogenated oils is inhibited by the addition of substances such as phenols, hydroquinone, pyrogallol, aluminum sulphate and zinc chloride. French P. 775,677, 1935, to International Hydrogenation Patents Co.; *Chem. Abs.*, 1935, **29**, 2734.

[56] E. W. J. Mardles, *Proc. World Petr. Congr.*, 1933, **2**, 57; *Brit. Chem. Abs.* **B**, 1934, 867; *J. Inst. Pet. Tech.*, 1934, **20**, 160A; *Chem. Abs.*, 1934, **28**, 4878.

[57] R. C. Bickmore, *Chem. Ind. (New York)*, 1934, **35**, 407; *Chem. Abs.*, 1935, **29**, 2721; *Brit. Chem. Abs.* **B**, 1935, 1031.

[58] A. Degtyarèva, *Azer. Neft. Khoz.*, **1934**, No. 2, 81; *Chem. Abs.*, 1934, **28**, 7504.

[59] F. Sager, *J. Inst. Pet. Tech.*, 1934, **20**, 1044; *Chem. Abs.*, 1935, **29**, 1236; *Brit. Chem. Abs.* **B**, 1935, 178; *J. Inst. Pet. Tech.*, 1935, **21**, 19A. Also French P. 775,762, 1935, to Aktiebolaget Separator-Nobel; *Chem. Abs.*, 1935, **29**, 3150.

[60] C. D. Lowry and C. G. Dryer, British P. 410,115, 1934, to Universal Oil Products Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 458A. Dutch P. 63,310, 1932, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech.*, 1935, **21**, 175A. *Cf.* also E. Vellinger and G. Radulesco, *Compt. rend.*, 1935, **200**, 1858; *Chem. Abs.*, 1935, **29**, 4920; *Brit. Chem. Abs.* **B**, 1935, 210. C. D. Lowry, Jr., C. G. Dryer, J. C. Morrell and G. Egloff, *Oil Gas J.*, 1934, **33** (12), 8; *Chem. Abs.*, 1934, **28**, 7504; *J. Inst. Pet. Tech.*, 1934, **20**, 614A.

[61] J. C. Morrell and C. G. Dryer, U. S. P. 1,993,941, Mar. 12, 1935, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1936, 261. *Chem. Abs.*, 1935, **29**, 3150. British P. 444,894, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 267A; *Brit. Chem. Abs.* **B**, 1936, 681. French P. 779,563, 1935; *Chem. Abs.*, 1935, **29**, 5647.

[62] J. C. Morrell and C. G. Dryer, U. S. P. 2,010,029, Aug. 6, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 6417; *Brit. Chem. Abs.* **B**, 1936, 731.

[63] W. L. Benedict, U. S. P. 2,014,923 and 2,014,924, Sept. 17, 1935, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1936, 681.

Sloane and Wasson[64] recommended the addition of a naphthenic hydrocarbon which has a kauri-butanol value above 15 as a gum flux for any fuel with a high potential gum content. Phosphatides are proposed also as inhibitors.[65]

Aliphatic amines have been recommended by many investigators. Burk[66] suggested the formation of an amine *in situ* by the interaction of ethylene dichloride and ammonia in solution in the gasoline at temperatures above 200°F. The addition of 0.002 per cent or more of a polybutyl or amyl amine, or 0.05 per cent of di- or triethanolamine, has been suggested.[67]

Various derivatives of the lower aliphatic acids, such as the amino and oxamic acids, urethanes,[68] *p*-hydroxyacetonitrile[69] and *p*-hydroxyphenylglycine[70] have been proposed as inhibitors in motor fuel. Esters of dibasic acids, such as diethyl maleate and dibutyl phthalate, are reported to retard the deterioration of cracked gasoline.[71]

Diarylguanidines[72] and their salts with various aliphatic acids[73] have been added to gasoline as antioxidants. The salts may be employed also with higher boiling fractions, such as lubricating and transformer oils, containing unsaturated hydrocarbons. The addition of imides, e.g., succinimide, phthalimide or its ethyl or phenyl derivatives, to cracked hydrocarbon distillates containing high proportions of unsaturates has been suggested.[74] Other inhibitors include semicarbazides and solutions of them,[75] monoalkyl or monoaryl hydrazines, and also acyl derivatives of aliphatic amines, diamines and secondary amines,[76] and certain substituted aromatic amines[77] and amides.[78]

According to Whyte[79] 1 per cent of a cyclic ketone, such as cyclohexanone, will stabilize a benzene-gasoline fuel.

A solution of phenol in cresol has been added to the more unstable fraction of a cracked gasoline after the fraction had been refined separately.[80] The other fractions were then blended with the stabilized lighter fraction. Phenol, cresols, guaiacol, anthracene and phenanthrene have been reported as "anti-catalysts" to render gasoline "gum and cloud free."[81] Other phenolic compounds, such as benzyl-*p*-aminophenol, pyrogallol or α-naphthol,[82] xylenols,[83] or *ter*-alkylated phenols,[84] aminophenols,[85] tetra-alkylphenols,[86] diaminophenols,[87] cyclohexylaminophenols,[88] benzylaminophenol,[89] 5-benzylamino-2-cresol,[90] 5-amino-2-hydroxytoluene,[91] amino-phenolic compounds, as 8-amino-1,4,5-trihydroxy naphthalene,[92] acylaminophenols,[93] benzylmethyl-, dibenzyl-, benzylidene-, cinnamylidene- and *o*-chlorobenzylidene-amino-phenol[94] have been suggested as antioxidants. Benzylaminophenol is added to fuels rendered unstable by lead tetraethyl.[95] A method for adding benzylaminophenol (dissolved in alcohol) to motor fuels has been proposed by Wagner.[96] Amino- and amino-hydroxy-phenones[97] and certain ethers, such as *p*-methylamino-*p'*-amino diphenyl ether,[98] are reported to be inhibitors.

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[64] R. G. Sloane and J. I. Wasson, British P. 419,690, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 2694; *J. Inst. Pet. Tech.*, 1935, **21**, 65A; *Brit. Chem. Abs.* **B**, 1935, 181. Canadian P. 357,976, 1936, *Chem. Abs.*, 1936, **30**, 4662. French P. 775,937, 1935; *Chem. Abs.*, 1935, **29**, 3497. F. A. Howard, U. S. P. 2,068,857, Jan. 26, 1937.

[65] British P., 409,353, 1932, to Hanseatische-Muhlenwerke A.-G.; *Brit. Chem. Abs.* **B**, 1934, 567; *Chem. Abs.*, 1934, **28**, 6296; *J. Inst. Pet. Tech.*, 1934, **20**, 425A.

[66] R. E. Burk, Canadian P. 347,582, 1935, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 3148. *Cf.* also U. S. P. 1,919,825, July 25, 1933; *Brit. Chem. Abs.* **B**, 1934, 440.

[67] W. S. Calcott and I. E. Lee, U. S. P. 1,940,445, Dec. 19, 1933, to E. I. du Pont de Nemours & Co., *Chem. Abs.*, 1934, **28**, 1523; *Brit. Chem. Abs.* **B**, 1934, 919. Canadian P. 341,958, 1934; *Chem. Abs.*, 1934, **28**, 5655. The addition of ethanolamines has also been suggested by J. B. Rather, L. C. Beard, Jr., and O. M. Reiff, U. S. P. 1,989,528, Jan. 29, 1935, to Socony-Vacuum Oil Co.; *Chem. Abs.*, 1935, **29**, 1978.

[68] E. W. J. Mardles and W. Helmore, British P. 417,653, 1934; *Chem. Abs.*, 1935, **29**, 1232; *J. Inst. Pet. Tech.*, 1934, **20**, 618A.

[69] Of the type formula $HO \cdot C_6H_4 \cdot NH \cdot CR_2 \cdot CN$, in which R is either hydrogen or various alkyl or aralkyl groups. F. B. Downing, R. G. Clarkson and G. Wolff, U. S. P. 1,957,134, May 1, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 216; *Chem. Abs.*, 1934, **28**, 4220. British P. 424,582, 1933; *Chem. Abs.*, 1935, **29**, 5260. Canadian P. 350,399, 1935, to Canadian Industries Ltd.; *Chem. Abs.*, 1935, **29**, 5260; *J. Inst. Pet. Tech.*, 1935, **21**, 174A; *Brit. Chem. Abs.* **B**, 1935, 486.

[70] F. B. Downing and H. W. Walker, U. S. P. 1,962,435, June 12, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 4899; *Brit. Chem. Abs.* **B**, 1935, 343.

[71] A. O. Jaeger, U. S. P. 1,995,615, March 26, 1935, to American Cyanamid and Chemical Corp.; *Chem. Abs.*, 1935, **29**, 3150; *Brit. Chem. Abs.* **B**, 1936, 439.

[72] W. S. Calcott and I. E. Lee, U. S. P. 1,972,760, Sept. 4, 1934, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1934, **28**, 6561; *Brit. Chem. Abs.* **B**, 1935, 759.

[73] W. S. Calcott and H. W. Walker, U. S. P. 1,939,659, Dec. 19, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 1523; *Brit. Chem. Abs.* **B**, 1934, 869. British P. 404,033, 1934; *J. Inst. Pet. Tech.*, 1934, **20**, 332A.

[74] A. O. Jaeger, U. S. P. 1,941,689, Jan. 2, 1934, to Selden Co.; *Chem. Abs.*, 1934, **28**, 1852; *Brit. Chem. Abs.* **B**, 1934, 1000.

[75] R. E. Burk, Canadian P. 339,775, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1934, **28**, 2884.

[76] E. W. J. Mardles and W. Helmore, British P. 423,938, 1933; *Chem. Abs.*, 1935, **29**, 4571; *Brit. Chem. Abs.* **B**, 1935, 394; *J. Inst. Pet. Tech.*, 1935, **21**, 174A.

[77] C. P. Wilson, Jr., U. S. P. 2,054,276, Sept. 15, 1936; *Chem. Abs.*, 1936, **30**, 7838.

[78] A. O. Jaeger, U. S. P. 2,070,304, Feb. 9, 1937, to American Cyanamid and Chemical Corp.

[79] S. Whyte, U. S. P. 2,032,242, Feb. 25, 1936; *Chem. Abs.*, 1936, **30**, 2730.

[80] F. B. Thole and W. H. Thomas, British P. 408,229, 1934, to Anglo-Persian Oil Co.; *Chem. Abs.*, 1934, **28**, 5968; *J. Inst. Pet. Tech.*, 1934, **20**, 375A; *Brit. Chem. Abs.* **B**, 1934, 566.

Alkylated polyphenols,[99] such as 3,4-dihydroxy-*ter*-butylbenzene,[100] 1,2-dihydroxy-4-propylbenzene[101] 1,2-dihydroxy-4-cyclohexylbenzene[102] and octyl pyrogallol,[103] a hydroxyphenylazo-α-naphthol[104] phenylazocatechol,[105] *p*-nitrophenylazopyrogallol,[106] monochlorohydroquinone,[107] nitrosopolyhydroxybenzenes[108] and nitroso derivatives of naphthols, naphthylamines, aniline and phenol[109] have been proposed as inhibitors of gum formation. The addition of polyphenols such as catechol,[110] hydroquinone and pyrogallol,[111] either alone or in solution in cresol,[112] as well as their esters,[113] aromatic or aliphatic keto,[114] alkyl,[115] alkoxyl[116] and naphthenyl[117] derivatives have been recommended. Vapor-phase cracked gasoline may be stabilized by dihydroxybenzenes, pyrogallol, nicotine pyrogallate or alkyl gallates.[118]

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[81] A. P. Bjerregaard, U. S. P. 1,761,810, June 3, 1930, to Doherty Research Co.; *Chem. Abs.*, 1930, **24**, 3639; U. S. P. reissue 19,512, Apr. 2, 1935, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1935, **29**, 3509. See also, K. S. Kuruindin and M. P. Kochneva, *Khim. Tverdogo Topliva,* 1935, **6**, 647; *Chem. Abs.*, 1936, **30**, 8578.

[82] W. H. Hoffert and G. Claxton, *Gas u. Wasserfach,* 1933, 76, 704; *Chem. Abs.*, 1934, **28**, 289. *Petroleum Times*, 1934, **32**, 517; *J. Inst. Pet. Tech.*, 1935, **21**, 21A. *Proc. World Petr. Congr.*, 1933, **2**, 69; *J. Inst. Pet. Tech.*, 1934, **20**, 253A; *Brit. Chem. Abs.* **B**, 1934, 948. See also *14me Congr. chim. ind.*, Paris, 1934; *Chem. Abs.*, 1935, **29**, 6019. Such inhibitors are recommended particularly for motor benzol.

[83] F. B. Downing and H. W. Walker, U. S. P. 1,945,521, Feb. 6, 1934, to E. I. du Pont de Nemours & Co; *Chem. Abs.*, 1934, **28**, 2519; *Brit. Chem. Abs.* **B**, 1934, 1048.

[84] H. E. Buc, U. S. P. 2,031,930, Feb. 25, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 2363.

[85] P. J. Carlisle and C. R. Harris, Canadian P. 343,933, 1933, to Canadian Industries Ltd.; *Chem. Abs.*, 1934, **28**, 7517. Cf., C. P. Wilson, Jr., U. S. P. 2,052,859, 1936; *Chem. Abs.*, 1936, **30**, 7325.

[86] F. B. Downing and H. W. Walker, U. S. P. 2,014,200, Sept. 10, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1936, 917; *Chem. Abs.*, 1935, **29**, 7636.

[87] L. G. Story, U. S. P. 2,023,385, Dec. 3, 1935, to Texas Co.; *Chem. Abs.*, 1936, **30**, 847.

[88] C. W. Hannum, U. S. P. 2,000,283, May 7, 1935, to E. I. du Pont de Nemours & Co.; *Chem Abs.*, 1935, **29**, 4166; *Brit. Chem. Abs.* **B**, 1936, 486.

[89] T. H. Rogers and V. Voorhees, Canadian P. 339,268, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1934, **28**, 2507. Also Canadian P. 327,322, 1932; *Chem. Abs.*, 1933, **27**, 1159. See also German P. 631,670, 1936, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1937, **31**, 250.

[90] H. T. Bennett and L. G. Story, U. S. P. 2,053,511, Sept. 8, 1936, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1936, **30**, 7325.

[91] H. T. Bennett and L. G. Story, U. S. P. 2,053,512, Sept. 8, 1936, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1936, **30**, 7325.

[92] Of the type formula $(HO)_x\text{-}R\cdot NH_2$, where R is a polyvalent homocyclic aromatic condensed ring radical, substituted or unsubstituted, and x is a whole number equal to or greater than 1. H. W. Elley and H. W. Walker, U. S. P. 2,065,568, Dec. 29, 1936, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1937, **31**, 1194.

[93] H. P. Lankelma, U. S. P. 1,938,456, Dec. 5, 1933, to Standard Oil Co. of Ohio; *Chem. Abs.*, 1934, **28**, 1178; *Brit. Chem. Abs.* **B**, 1934, 870.

[94] C. W. Hannum, U. S. P. 1,980, 200 and 1,980,201, Nov. 13, 1934, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1935, **29**, 334; *Brit. Chem. Abs.* **B**, 1935, 937.

[95] R. E. Wilson, U. S. P. 2,004,560, June 11, 1935, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1935, **29**, 5260.

[96] C. R. Wagner, *Oil and Gas J.*, 1934, **32** (45), 59; *J. Inst. Pet. Tech.*, 1934, **20**, 322A.

[97] L. G. Story, U. S. P. 2,034,274, Mar. 17, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 3215. Canadian P. 352,532, 1935, to Texaco Development Corp.; *Chem. Abs.*, 1935, **29**, 7634.

[98] Of the type of formula (A)N(R)X(B) where A is alkyl, N is nitrogen, or imino, R is aryl or aralkyl with or without substituents, X is oxygen, sulphur, selenium or tellurium and B is alkyl, aryl, or mixed and may be substituted. British P. 430,335, 1935, to Wingfoot Corp.; *J. Inst. Pet. Tech.*, 1935, **21**, 344A.

[99] British P. 406,195, 1933, to Texaco Development Corp.; *Brit. Chem. Abs.* **B**, 1934, 354; *J. Inst. Pet. Tech.*, 1934, **20**, 332A.

[100] L. E. Mills and B. L. Fayerweather, U. S. P. 1,942,847, Jan. 9, 1934, to Dow Chemical Co.; *Brit. Chem. Abs.* **B**, 1934, 920.

[101] French P. 800,839, 1936, to Soc. des usines chimiques Rhône-Poulenc; *Chem. Abs.*, 1937, **31**, 242.

[102] L. E. Mills and B. L. Fayerweather, U. S. P. 2,044,318, June 16, 1936, to Dow Chemical Co.; *Chem. Abs.*, 1936, **30**, 5405.

[103] E. G. Borden, U. S. P. 2,047,355, July 14, 1936, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1936, **30**, 6184.

[104] C. D. Lowry, Jr., U. S. P. 2,051,871, Aug. 25, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 6938.

[105] C. D. Lowry, Jr., U. S. P. 2,051,872, Aug. 25, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 6938.

Polyamines, such as *o*- and *p*-phenylenediamine,[119] tolylenediamines,[120] diaryl arylenediamines[121] and diaminodiphenylamine,[122] are said to be effective antioxidants. Gasoline which has been partly refined with sulphuric acid may be protected from oxidation by the addition of substances containing an aromatic polyamine radical.[123]

Pyridine or picolines,[124] phenoxazine,[124a] azoxybenzene, hydrazobenzene,[125] aminoazo- and hydroxyazo-benzenes[126] have been proposed as gum inhibitors.

Ayres[127] has suggested the use of triphenyl phosphate, benzidine, α-naphtholbenzein, xylidine, and lead or calcium sucrate. Amine salts of hydroxy aromatic hydrocarbons have also been proposed.[128]

A solution of α-naphthol and aniline in ether prevents deterioration of cracked gasoline.[129] The addition of α-naphthol and phenyl-β-naphthylamine to a motor fuel not only retards the induction period but also lowers the rate of gum formation.[130] Dihydroxynaphthalenes,[131] 1,4-dihydroxyanthraquinone,[132] 1,2-dihydroxyanthraquinone,[133] α-naphthol and α-naphthylamine, aryl-amino-naphthalenes,[134] acetone anil,[135] aldol-α-naphthylamine[136] and 1,8-epoxynaphthalene[137] are gum inhibitors.

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[106] C. D. Lowry, Jr., U. S. P. 2,051,873, Aug. 25, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 6938.

[107] L. A. Clarke and C. C. Towne, U. S. P. 2,023,871, Dec. 10, 1935, to Texas Co.; *Chem. Abs.*, 1936, **30**, 851.

[108] C. Winning, U. S. P. 1,982,277, Nov. 27, 1934, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1935, **29**, 595; *Brit. Chem. Abs.* **B**, 1935, 484.

[109] T. H. Rogers and V. Voorhees, U S. P. 1,982,267 and 1,982,618, Nov. 27, 1934, to Gasoline Antioxidant Co.; *Brit. Chem. Abs.* **B**, 1935, 984; *Chem. Abs.*, 1935, **29**, 579, 595.

[110] H. T. Bennett and L. G. Story, U. S. P. 2,038,630, Apr. 28, 1936, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1936, **30**, 4313.

[111] W. K. Lewis and B. Mead, U. S. P. 1,996,075, Apr. 2, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 3509; *Brit. Chem Abs.* **B**, 1936, 358.

[112] French P. 760,011, 1934, to Anglo-Persian Oil Co.; *Chem. Abs.*, 1934, **28**, 3579.

[113] L. A. Clarke and H. Levin, U. S. P. 2,034,283, Mar. 17, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 3222. Also French P. 759,398, 1934, to Texaco Development Corp.; *Chem. Abs.*, 1934, **28**, 3579.

[114] L. A Clarke, U. S. P. 2,034,024, Mar. 17, 1936, to Texas Co.; *Chem. Abs.*, 1936, 30, 3206; Canadian P. 349,641, 1935, to Texaco Development Corp.; *Chem Abs.*, 1935, **29**, 4166.

[115] J. B. Rather, L. C. Beard, Jr. and O. M. Reiff, U. S. P. 1,959,315, May 15, 1934, to Socony-Vacuum Corp.; *Chem Abs.*, 1934, **28**, 4587; *Brit. Chem. Abs.* **B**, 1935, 217.

[116] W. S. Calcott and I. E. Lee, U. S. P. 1,999,830, Apr. 30, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 4166.

[117] C. G. Ludeman, U. S. P. 1,994,891, Mar. 19, 1935, to Texas Co.; *Chem. Abs.*, 1935, **29**, 3149; *Brit. Chem Abs.* **B**, 1936, 261.

[118] T H. Rogers and V. Voorhees, U. S. P. 1,970,339, Aug. 14, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1934, **28**, 6296; *Brit. Chem. Abs.* **B**, 1935, 662.

[119] H. T. Bennett and L. G. Story, U. S. P. 2,038,631 and 2,038,632, Apr. 28, 1936, to Gasoline Antioxidant Co.; *Chem Abs.*, 1936, **30**, 4313.

[120] W. S. Calcott and H. W. Walker, U. S. P. 1,971,329, Sept. 28, 1934, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1934, **28**, 6561; *Brit. Chem. Abs.* **B**, 1935, 713.

[121] P. I. Murrill, U. S. P. 1,947,219, Feb. 13, 1934, to R. T. Vanderbilt Co.; *Chem. Abs.*, 1934, **28**, 2519; *Brit. Chem. Abs.* **B**, 1934, 1048.

[122] T. W. Bartram, U. S. P. 2,032,787, Mar. 3, 1936, to Monsanto Chemical Co.; *Chem. Abs.*, 1936, **30**, 2747.

[123] T. H. Rogers and V. Voorhees, Canadian P. 339,269, 1934, to Standard Oil Co. of Ind.; *Chem. Abs*, 1934, **28**, 2507.

[124] J. W. Orelup, U. S. P. 1,909,069, May 16, 1933, to Patent Fuels and Color Corp.; *Brit. Chem. Abs.* **B**, 1934, 183.

[124a] T. W. Bartram, U. S. P. 2,062,201, Nov. 24, 1936, to Monsanto Chemical Co.; *Chem. Abs.*, 1937, **31**, 851.

[125] E. W. McMullan, U. S. P. 2,027,394, Jan. 14, 1936, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1936, **30**, 1553.

[126] T. H. Rogers and V. Voorhees, U. S. P. 2,030,940, Feb. 18, 1936, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1936, **30**, 2363.

[127] E. Ayres, British P. 406,658, 1932, to Gulf Refining Co.; *Brit. Chem Abs.* **B**, 1934, 441; *J. Inst. Pet. Tech.*, 1934, **20**, 332A. Canadian P. 348,174, 1935; *Chem. Abs.*, 1935, **29**, 3509.

[128] F. B. Downing and H. W. Walker, British P. 398,219, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 1509. Canadian P. 342,593, 1934; *Chem. Abs.*, 1934, **28**, 5975.

[129] J. P. Smoots, Canadian P. 355,372, 1936, to Standard Oil Co. of Ohio; *Chem. Abs.*, 1936, **30**, 2363. U. S. P. 2,065,249, Dec. 22, 1936; *Chem. Abs.*, 1937, **31**, 1194.

Some of the higher hydrocarbons, such as anthracene and phenanthrene, are antioxidants.[138] Gum formation in fuels which are rendered unstable by organometallic compounds may be inhibited by the addition of naphthols, naphthylamines, polyhydroxybenzenes,[139] hexadecylphenyl acetylene,[139a] dinaphthylene oxide or dioxide or perylene.[140] Amino and hydroxy derivatives of phenanthrene, chrysene, picene,[141] dihydroxy, dihalo, dicyano and dibenzyl derivatives of perylene[142] and diamino and dihydroxy derivatives of fluorene[143] have been used to inhibit autoxidation. The following substances have also been suggested: camphor, camphorone, camphoric acid,[144] hydroxyquinolines, hydroxytetrahydroquinolines,[145] thiodiarylamines,[146] substituted aryl arsine or stibine oxides[147] and N-(hydroxyaryl)-morpholines,[148] unrefined corn oil,[149] nascent hydrogen[150] and aliphatic-amine salts of hydroxy-aryl compounds as hydroquinone dianilide.[151]

[130] E. Ayres, U. S. P. 2,048,770, July 28, 1936, to Gulf Oil Corp.; *Chem. Abs.*, 1936, **30**, 6184.

[131] F. B. Downing and H. W. Walker, U. S. P. 2,025,192, Dec. 24, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 1223. British P. 432,121, 1935; *Chem Abs.*, 1936, **30**, 279; *Brit. Chem. Abs.* **B**, 1935, 838; *J. Inst. Pet. Tech.*, 1935, **21**, 381A.

[132] J. W. Orelup, U. S. P. 2,016,648, Oct. 8, 1935; *Chem. Abs.*, 1935, **29**, 8319.

[133] R. E. Burk and H. P. Lankelma, U. S. P. 2,053,421, Sept. 8, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 7325

[134] H. G. M. Fischer and C. E. Gustafson, U. S. P. 2,004,094, June 11, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 4933. U. S. P. 2,019,899, Nov. 5, 1935, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1936, **30**, 607. J. B. Rather, L. C. Beard, Jr., and O. M. Reiff, U. S. P. 2,062,675, Dec. 1, 1936, to Socony-Vacuum Oil Co; *Chem. Abs.*, 1937, **31**, 838. Phenyl-α-naphthylamine has been suggested to prevent deterioration of motor benzol prepared from destructive distillation of bituminous materials. T. H. Rogers and V. Voorhees, Canadian P. 339,267, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1934, **28**, 2507. See also, R. Carrozzi [*Rev. facultad cienc. quim. (Univ. La Plata)*, 1935, **10**, 61; *Brit. Chem. Abs.* **B**, 1936, 966; *Chem. Abs.*, 1936, **30**, 7317] in connection with aviation gasoline.

[135] Of the general formula $(R)_2C{=}NX$ where R is an aliphatic or aromatic hydrocarbon radical and X is an aromatic hydrocarbon radical. T. W. Bartram U. S. P. 2,055,810, Sept. 29, 1936, to Monsanto Chemical Co.; *Chem. Abs*, 1936, **30**, 8599.

[136] C. D. Lowry, Jr., and C. G. Dryer, U. S. P. 1,924,870, Aug. 29, 1933, to Universal Oil Products Co.; *Chem. Abs.*, 1933, **27**, 5531; *Brit. Chem Abs.* **B**, 1934, 567

[137] This is formed by oxidizing α-naphthol with 20 per cent ferric chloride. E. Ayres, U. S. P. 1,991,779, Feb. 19, 1935, to Gulf Refining Co., *Brit. Chem. Abs* **B**, 1936, 87, *Chem Abs*, 1935, **29**, 2349. British P. 399,733, 1933; *Chem. Abs*, 1934, **28**, 1853. Canadian P. 348,175, 1935; *Chem Abs.*, 1935, **29**, 3509.

[138] A. P. Bjerregaard, U. S. P. 1,949,896, Mar. 6, 1934, to Gasoline Antioxidant Co.; *Brit Chem Abs.* **B**, 1935, 180.

[139] R. E. Wilson, Canadian P. 351,879, 1935, to Standard Oil Co.; *Chem. Abs*, 1935, **29**, 7066.

[139a] R. G. Sloane and J. I. Wasson, U. S. P. 2,066,234, Dec. 29, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1937, **31**, 1183.

[140] J. W. Orelup, British P. 420,371, 1933; *Brit. Chem. Abs.* **B**, 1935, 136; *J. Inst. Pet. Tech*, 1935, **21**, 66A.

[141] L. G. Story, Canadian P. 349,645, 1935, to Texaco Development Corp.; *Chem. Abs.*, 1935, **29**, 4166.

[142] F. Kuhrmann, German P. 614,065, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 8381; *J. Inst. Pet. Tech.*, 1935, **21**, 312A.

[143] L. G. Story, U. S. P. 2,018,979, Oct. 29, 1935, to Texas Co.; *Chem. Abs.*, 1936, **30**, 281; *Brit. Chem. Abs.* **B**, 1936, 630.

[144] J. C. Morrell, U. S. P. 1,930,248, Oct. 10, 1933, to Universal Oil Products Co.; *Chem. Abs.*, 1934, **28**, 313; *Brit. Chem. Abs.* **B**, 1934, 615.

[145] E. B. McConnell, U. S. P. 2,030,033, Feb 4, 1936, to Standard Oil Co. of Ohio; *Chem. Abs*, 1936, **30**, 1990.

[146] T. W. Bartram, U. S. P. 2,006,756, July 2, 1935, to Rubber Service Laboratories Co.; *Chem. Abs.*, 1935, **29**, 5646.

[147] A. L. Blount, U. S. P. 2,013,198, Sept. 3, 1935, to Union Oil Co. of Calif.; *Chem. Abs.*, 1935, **29**, 7066.

[148] F. B. Downing and R. G. Clarkson, British P. 444,585, 1936, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1936, 681; *J. Inst. Pet. Tech.*, 1936, **22**, 266A. Canadian P. 352,906, 1935, to Canadian Industries Ltd.; *Chem. Abs.*, 1935, **29**, 8319. *Cf.* Canadian P. 342,768, 1934; *Chem. Abs.*, 1934, **28**, 6295.

[149] C. D. Lowry, Jr., U. S. P. 2,014,235, Sept. 10, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 7636; *Brit. Chem. Abs.* **B**, 1936, 917.

[150] When gasoline is to be stored for a long period, generation occurs beneath and an atmosphere of hydrogen is maintained above the surface of the gasoline. H. C. Weber, U. S. P. 2,029,748, Feb. 4, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 1992.

[151] F. B. Downing and H. W. Walker, U. S. P. 2,053,466, Sept. 8, 1936, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1936, **30**, 7313.

It has been found that petroleum distillates can be stabilized in the vapor phase at about 300-500°C. in contact with catalysts of sulphides, selenides or tellurides of metals from groups 6 to 8 of the Periodic Table.[152]

Dyestuffs of several types, such as dyes of the oxazine-, indamine-, eurhodine-, safranone- or aposafranone-base groups, have been used in conjunction with amino or phenolic inhibitors in gasoline of normal gum-forming character.[153] Ayers[154] has proposed to treat the gasoline with an adsorptive polymerization catalyst and subsequently add an aminobenzene. Complex condensation products, such as those formed from di-α-naphthylamine and cresol[155] or from a quinone, phenol or naphthol and an aryl amine, diamine or aminophenol,[156] or from an aliphatic ketone and a phenol,[157] are inhibitors. The reaction product of an olefin with a wood tar distillate boiling between 240-280°C. also has been employed.[158] An inhibitor may be added before or during the condensation of the fuel,[159] and more may be added subsequently. A color neutralizer may be incorporated simultaneously.[160]

EVALUATION OF INHIBITORS

Evaluation of the antioxidant effect of various inhibitors has been studied by Dryer and co-workers.[161] They recommended that antioxidant power be given as the "cyclohexene number," which is defined as the number of minutes that the induction period of pure cyclohexene, as determined in accelerated oxidation tests, will be retarded by 0.002 per cent of the substance under investigation. Instead of determining the cyclohexene number directly on the pure hydrocarbon, these investigators thought it better to use reference fuels. Gasolines from several sources were correlated with cyclohexene in respect to stability by using α-naphthol as an inhibitor. These were then blended with straight-run gasoline in such proportions that the final mixture required five times as much inhibitor to produce the same induction period as that exhibited by cyclohexene. Even when the quantity of added inhibitor was varied over a wide range, the correlation between the induction periods of these reference fuels and those exhibited by cyclohexene was fairly constant. This is shown in Fig. 206.

Because the inhibitors investigated were not very soluble directly in gasoline, liquids were sought which could be used as solvents (thus aiding dissolution of the inhibitor in the fuel) and at the same time not influence the results. Benzene and Hexone (methyl isobutyl ketone) were chosen as they filled the requirements satisfactorily. Cyclohexene numbers which were determined by these workers are given in Table 189.

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[152] French P. 799,813, 1936, Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 8594.

[153] C. Winning, L. E. Sargent and J. F. Dudley, U. S. P. 2,031,917, Feb. 25, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 2363.

[154] G. W. Ayers, Jr., U. S. P. 2,039,576, May 5, 1936, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1936, **30**, 4313.

[155] E. Ayres and M. L. Hill, U. S. P. 2,027,462, Jan. 14, 1936, to Gulf Refining Co.; *Chem. Abs.*, 1936, **30**, 1553.

[156] L. P. Chebotar, U. S. P. 1,913,370, June 13, 1933, to Texas Co.; *Brit. Chem. Abs.* **B**, 1934, 184. Canadian P. 350,765, 1935; *Chem. Abs.*, 1935, **29**, 5260. This condensation product is formed *in situ*.

[157] W. J. Bannister, U. S. P. 2,017,827, Oct. 15, 1935, to Commercial Solvents Corp.; *Chem. Abs.*, 1935, **29**, 8319; *Brit. Chem. Abs.* **B**, 1936, 630.

[158] V. N. Ipatieff, U. S. P. 2,058,881, Oct. 27, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1937, **31**, 250.

[159] German P. 615,420, 1935, to Carbo-Norit Union Verwaltungs-Ges.m.b.H.; *Chem. Abs.*, 1935, **29**, 6405.

[160] French P. 775,323, 1934, to Carbo-Norit Union Verwaltungs-Ges.m.b.H.; *Chem. Abs.*, 1935, **29**, 2695.

[161] C. G. Dryer, C. D. Lowry, Jr., G. Egloff and J. C. Morrell, *Ind. Eng. Chem.*, 1935, **27**, 315; *Brit. Chem. Abs.* **B**, 1935, 535; *J. Inst. Pet. Tech.*, 1935, **21**, 203A; *Chem. Abs.*, 1935, **29**, 2714. The color reactions of various antioxidants with concentrated sulphuric acid have been determined by H. Endo, *J. Soc. Chem. Ind. Japan*, 1935, **38**, Suppl. binding, 618; *Chem. Abs.*, 1936, **30**, 2042; *Brit. Chem. Abs.* **B**, 1936, 181.

TABLE 189.—*Cyclohexene Numbers.*

Substance	Cyclohexene Number
p-Aminophenol	1400
2-Amino-5-hydroxytoluene	1020
Benzyl-*p*-aminophenol	935
p-Hydroxyphenylmorpholine	935
Dibenzyl-*p*-aminophenol	915
Pyrogallol	845
1,5-Dihydroxynaphthalene	820
Catechol	745
α-Naphthol	610
2,4-Diaminodiphenylamine	600
p,p'-Diaminodiphenylamine	595
Thiodiphenylamine	535
p-Phenylenediamine	475
o-Aminophenol	415
p-Aminodiethylaniline	325
o-Phenylenediamine	310
Hydroquinone monomethyl ether	280
4-Chloro-2-aminophenol	200
4-Hydroxy-1,2-dimethylbenzene	185
m-Aminophenol	185
Phenyl-α-napthylamine	185
2-Hydroxy-1,3-dimethylbenzene	175
2-Amino-4-nitrophenol	175
Pyrogallol dimethyl ether	150
Heptylresorcinol	140
Hexylresorcinol	140
2-Hydroxy-1,4-dimethylbenzene	130
Thymol	125
m-Tolylenediamine	120
4-Hydroxy-1,2-dimethylbenzene	110
m-Phenylenediamine	105
Butylguaiacol	100
Gallic acid	85
Orcinol	65
Resorcinol monoethyl ether	65
Resorcinol	55
Resorcinol monomethyl ether	55
Isoeugenol	50
Eugenol	50
5-Hydroxy-1,3-dimethylbenzene	35
β-Naphthol	35

Lowry and his collaborators[162] have suggested that it is possible to determine the inhibiting power of a substance by measurement of its critical oxidation potential. This is defined, for phenols and amines, as "the potential of some oxidizing solution which will cause a certain small amount of the amine or phenol to become oxidized in 5 minutes when equivalent amounts of the sample and of the oxidizing agent are employed."[163] Lowry and his co-workers also found that there was maximum inhibiting action shown by substances which gave a critical oxidation potential of between 0.600 and 0.800 volt. Their data are shown graphically in Fig. 207.

Dryer and collaborators[164] have investigated the storage stability of cracked gasoline as related to its induction period and the critical oxidation potential of added inhibitors. They used equimolecular amounts of various inhibitors. Part of the data they obtained is given in Table 190.

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[162] C. D. Lowry, Jr., G. Egloff, J. C. Morrell and C. G. Dryer, *Ind. Eng. Chem.*, 1933, 25, 804.

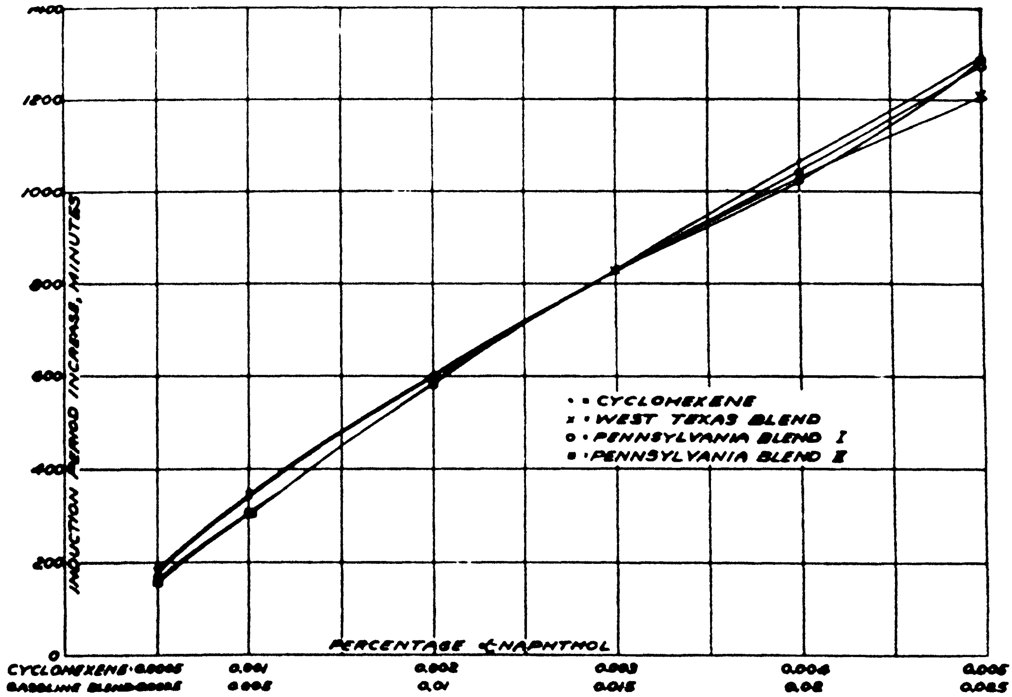
[163] L. F. Fieser, *J.A.C.S.*, 1930, 52, 5204.

[164] C. G. Dryer, J. C. Morrell, G. Egloff and C. D. Lowry, Jr., *Ind. Eng. Chem.*, 1935, 27, 15; *Chem. Abs.*, 1935, 29, 4559; *Brit. Chem. Abs.* B, 1935, 582; *J. Inst. Pet. Tech.*, 1935, 21, 93A.

TABLE 190.—*Correlation of Critical Oxidation Potential and Effectiveness in Storage.*

Inhibitor	Critical Oxidation Potential Volts	Induction Period Minutes	Time to Reach Peroxide No. of 1	2	5	Air-Jet Gum of 10 mg.	15 mg.
			Months			Months	
None		60	1	2	3	2+	6+
Hydroquinone	0.631	80	4.5	5	6	6	2
Catechol	0.742	130	2.5	3	4	4	4
Pyrogallol	0.609	265	17	17	17	17	17
α-Naphthol	0.797	170	8	9	10	9	9
2-Hydroxy-1,3-dimethylbenzene	0.895	95	1	2	3	3	3
p-Cresol	1.038	80	1	2	3	2	3
Phenol	1.089	80	1	2	2	2	3
Aniline	1.135	90	1	2	3	3	3

These results indicate that the most efficient inhibitors were those with oxidation potentials in the maximum range, that is, 0.600 to 0.800 volt.

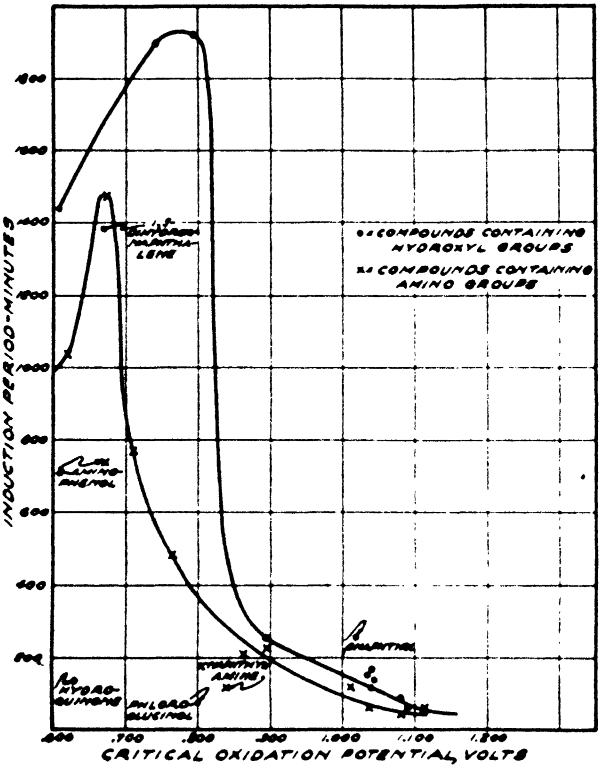


Courtesy Industrial and Engineering Chemistry

FIG. 206.—Comparison of Cyclohexene and Gasoline Blends as Standards for Evaluation of Oxidation Inhibitors. (C. G. Dryer, C. D. Lowry, Jr., G. Egloff and J. C. Morrell)

MECHANISM OF GUM FORMATION

It is well known that peroxides are intermediates in gum formation. Aldehydes and acids are also formed but they are present only as secondary products, according to Dryer and co-workers.[165] These investigators studied gasoline from several sources and concluded that the addition of inhibitors checked not only the development of gum, but also of peroxides, aldehydes and acids as well.[166] The results indicated that in all probability these oxygenated bodies are derived from the same source. The influence of various factors, such as the presence of different types of unsaturated substances and the effect of ultraviolet light, on peroxide and gum formation has been widely discussed.[167] Aromatic hydrocarbons with unsaturated side chains yield peroxides and are oxidized readily. However, Candea and Cristodulo[168] found that the high aromatic content of motor fuels derived from Rumanian



Courtesy Industrial and Engineering Chemistry

FIG. 207.—Correlation Between Induction Period and Critical Oxidation Potential for Compounds Containing Hydroxyl and Amino Groups. (C. D. Lowry, Jr., G. Egloff, J. C. Morrell and C. G. Dryer)

crude oils prevented any considerable peroxide formation. With a gasoline from Moreni crude oil, they observed[169] that cyclohexane and pinene promoted peroxide formation although the aromatic hydrocarbons present were not readily oxidized. Pipik and Mezhebovskaya[170] studied the influence of refining methods on the storage stability of gasoline. They noted that peroxides could be removed by treating the vapors of the fuel with floridin earth, and further formation prevented by the addition of an inhibitor immediately after refining.

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[165] C. G. Dryer, C. D. Lowry, Jr., J. C. Morrell and G. Egloff, *Ind. Eng. Chem.*, 1934, **26**, 885; *Chem. Abs.*, 1934, **28**, 5973; *J. Inst. Pet. Tech.*, 1934, **20**, 490A; *Brit. Chem. Abs.* **B**, 1934, 948.

[166] For a theory of autoxidation of oxygen-containing compounds, such as alcohols, see N. A. Milas, *Chem. Rev.*, 1932, **10**, 295. Also, W. P. Jorissen and P. A. A. van der Beek, *Rec. trav. chim.*, 1927, **46**, 42; *Chem. Abs.*, 1927, **21**, 1582; *Brit. Chem. Abs.* **A**, 1927, 326.

[167] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934. Also T. Zamfirescu, *Analele minelor România*, 1932, **15**, 177; *Chem. Abs.*, 1934, **28**, 4863. E. Norlin, *Tek. Tid. Uppl. C. Kemi*, 1933, **63**, 89; *Chem. Abs.*, 1934, **28**, 1849. A. A. Vuoreia (*Suomen Kemistilehti*, 1935, **8A**, 115; *Chem. Abs.*, 1936, **30**, 602) discusses the role played by peroxides. See also M. N. Mikhailova and M. B. Neiman, *J. Gen. Chem.* (*U.S.S.R.*), 1936, **6**, 821; *Chem. Abs.*, 1936, **30**, 7016; *Brit. Chem. Abs.* **A**, 1936, 1211.

[168] C. Candea and N. Cristodulo, *Chim. et ind.*, 1934, **31**, Spec. No. 374; *Brit. Chem. Abs.* **B**, 1934, 662.

Morrell and his collaborators have confirmed the belief that diolefins and olefins are essential for peroxidation.[171] They also showed that a mixture of olefins had a greater tendency to form gum than any of its components separately. The degree of oxidizability of various hydrocarbons (or mixtures of these) was measured by the peroxide number and gum content (air-jet method) before and after oxidation for 4 hours at 100°C. and 100 pounds pressure. In addition the induction period was also determined. Some of the data obtained in this manner are given in Table 191.

TABLE 191.—*Oxidation of Pure Hydrocarbons.*

	Before Oxidation		After 4 Hours Oxidation		
Substance	Peroxide Number	Air-Jet Gum (mg. per 100 cc.)	Peroxide Number	Air-Jet Gum (mg. per 100 cc.)	Induction Period (in min.)
Paraffins					
n-Heptane	0.06	0	0.22	0	No break
n-Octane	0.09	0	0.79	0	" "
2,2,4-Trimethyl pentane	0.06	0	0.03	0	" "
Aromatics					
Benzene	0.02	0	0.03	2	" "
Toluene	0.00	1	0.30	2	" "
Olefins					
2-Octene	0.00	0	240	44	150
2-Pentene	0.00	0	192	22	90
Trimethyl ethylene	0.00	1	138	10	75
Cyclohexane	0.02	0	0.19	0	No break
Cyclohexene	0.06	1	240	290	75
Indene	0.25	294	15.2	17	30
Limonene	0.10	8	240	1734	30
Indene (20%) *n*-Heptane (80%)	0.19	-	5.5	—	60
Blended (in per cent indicated) with Pennsylvania straight-run gasoline					
n-Heptane (20%)	0.00	0	0.09	0	No break
Cyclohexene (20%)	0.06	1	48	4	" "
Styrene (2%)	0.06	0	1.59	0	" "
Cyclohexene (20%) Styrene (1%)	1.9	0	140	50	180
Isoprene (2%)	0.12	0	18	34	No break
Isoprene (3.9%)	0.12	0	86	250	105
Cyclohexene (20%) Isoprene (1%)	0.45	0	220	122	120
Straight-run gasoline alone	0.0	0	0.12	0	No break

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[169] C. Candea and N. Cristodulo, *Bull. soc. école polytech. Timisoara*, 1934, **5**, 233; *Brit. Chem. Abs.* **B**, 1936, 356.

[170] O. Pipik and E. Mezhebovskaya, *Azer. Neft. Khoz.*, 1935, **15** (9), 58; *Chem. Abs.*, 1936, **30**, 6544. Translation in *Oil Gas J.*, 1936, **35** (9), 50; *Chem. Abs.*, 1936, **30**, 7828; *J. Inst. Pet. Tech.*, 1936, **22**, 508A.

[171] J. C. Morrell, C. G. Dryer, C. D. Lowry, Jr., and G. Egloff, *Ind. Eng. Chem.*, 1934, **26**, 655; *Chem. Abs.*, 1934, **28**, 5648; *Brit. Chem. Abs.* **B**, 1934, 707; *J. Inst. Pet. Tech.*, 1934, **20**, 450A.

Peroxide number is defined, according to Yule and Wilson,[172] as the gram equivalents of active oxygen per 1000 liters of sample. This is estimated by determining the quantity of ferrous sulphate, dissolved in aqueous acetone, oxidized by 10 cc. of the sample under investigation.[173]

As a result of their studies on the effect of peroxide formation on a cracked gasoline, Morrell and his co-workers[174] found that an increase in peroxide concentration resulted in an increase in color and gum formation and a decrease in antiknock value and susceptibility to inhibitors. They also noted that the rate of peroxide formation and response to inhibitors were closely related.

Vellinger and Radulesco[175] report that the rate of gum formation in cracked gasoline is accelerated on exposure of the liquids (in quartz tubes) to ultraviolet light. However, they believed that oxygen was necessary for the development of gum, whether or not the latter occurred in the light or in the dark. It was observed that the hydrocarbons responsible for gumming were destroyed by chromic acid. Aside from olefins which form peroxides, the acetylenic hydrocarbons (which are either liquids or have been melted) also form peroxides.[176] Although this may be due to polymerization of the acetylenes to olefins which can then react with oxygen, it seems more probable that the acetylenes form peroxides directly. The alkyl acetylenes react more readily than the aryl derivatives, but acetylene itself does not seem to form a peroxide.

Morrell, Benedict and Egloff investigated the effect of light on gasoline[177] and on pure hydrocarbons.[178] In order to ascertain the effect of various conditions on the stability of the gasoline to color and gum formation, experiments were carried out on straight-run and cracked gasoline as well as a blend of these two. Elemental sulphur, *n*-propyl disulphide and both of these substances were added to different samples and the latter exposed to a carbon-arc light for 60 minutes while different gases, such as nitrogen, hydrogen, oxygen and carbon dioxide, were bubbled through the samples. In this way it was possible to get a large number of different conditions ranging from a sample with no added sulphur compounds in an inert atmosphere (such as nitrogen or carbon dioxide) to one containing sulphur and *n*-propyl disulphide in an atmosphere of oxygen. Part of the data which were obtained for gasolines are shown in Table 192.

It was observed that unsaturated hydrocarbons behaved similarly to cracked gasoline, and that in general the results for gasolines were the summation of the results for the constituent pure hydrocarbons. The presence of elementary sulphur or organic disulphides apparently makes for color instability. The haze formed in gasoline by the oxidation of sulphur was found to contain most of the acid. Gum formed, even in the absence of oxygen, but there was no fixed relationship between gum and color.

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[172] S. A. C. Yule and C. P. Wilson, Jr., *Ind. Eng. Chem.*, 1931, **23**, 1254. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[173] This method has been modified somewhat so that acetone is replaced by absolute methanol. The ferrous sulphate is oxidized in the presence of ammonium thiocyanate and the resulting quantity of red ferric thiocyanate determined by colorimetric comparison with similar solutions of known concentration. C. A. Young, R. R. Vogt and J. A. Nieuwland, *Ind. Eng Chem., Anal. Ed.*, 1936, **8**, 198; *J. Inst. Pet. Tech.*, 1936, **22**, 345A. P. L. Burnin, N. G. Worton and E. E. Bibbins (*J. Am. Pharm. Assoc.*, 1936, **25**, 27; *Chem. Abs.*, 1936, **30**, 2702) have estimated the stability of mineral oil by determining the peroxides formed after aging under 20 pounds steam pressure for 1 hour. They used a ferrous-sulphate-potassium-thiocyanate test solution in their analyses.

[174] J. C. Morrell, C. G. Dryer, C. D. Lowry, Jr., and G. Egloff, *Ind Eng. Chem.*, 1934, **26**, 497; *Chem. Abs.*, 1934, **28**, 4878; *Brit. Chem. Abs.* **B**, 1934, 612; *J. Inst. Pet. Tech.*, 1934, **20**, 358A.

[175] E. Vellinger and G. Radulesco, *Ann. combustibles liquides*, 1934, **9**, 901; *J. Inst. Pet. Tech.*, 1935, **21**, 17A. *Proc. World. Petr. Congr.*, 1933, **2**, 103; *Brit Chem. Abs.* **B**, 1934, 819; *J. Inst. Pet. Tech.*, 1934, **20**, 97A. *Ann. combustibles liquides*, 1933, **8**, 883; *Chem. Abs.*, 1934, **28**, 621.

[176] C. A. Young, R. R. Vogt and J. A. Nieuwland, *J.C.S.*, 1935, 115; *Brit. Chem. Abs.* **A**, 1935, 325; *Chem. Abs.*, 1935, **29**, 1771.

[177] J. C. Morrell, W. L. Benedict and G. Egloff, *Ind. Eng. Chem.*, 1936, **28**, 122; *Chem. Abs.*, 1936, **30**, 2738; *Brit. Chem. Abs.* **B**, 1936, 307.

[178] J. C. Morrell, W. L. Benedict and G. Egloff, *Ind. Eng. Chem*, 1936, **28**, 448; *Chem. Abs.*, 1936, **30**, 3979; *J. Inst. Pet. Tech.*, 1936, **22**, 254A.

TABLE 192.—*Effect of Light on Gum Formation*
(Air-Jet Gum in Mg. per 100 cc.)

	Type of Gasoline								
	Straight-Run			Cracked			Blended		
Atmosphere	Air	O_2	CO_2	Air	O_2	CO_2	Air	O_2	CO_2
Compound added									
None	6	10	2	4	15	2	5	16	2
Sulphur (0.01%)	10	24	5	15	34	5	16	36	6
n-Propyl disulphide	7	14	2	5	20	1	5	20	2
n-Propyl disulphide plus sulphur	12	19	0	13	26	2	11	25	0

The amount of *n*-propyl disulphide used corresponded to 0.10 per cent sulphur.

COLOR STABILITY OF PETROLEUM DISTILLATES

Hillman[179] has classified the types of color instability of kerosene:

1. Clear lemon-yellow which appears in the dark and is an oxidation effect due to various types of compounds, especially unsaturated naphthenic acids.
2. A similar type due to amino-bodies.
3. Discoloration caused by cracked bodies.
4. A gradual brownish coloration due to age and light.

An indication of the color stability is given by the Hillman test which consists of agitating 700 cc. of kerosene for 60 seconds with 1 g. of standard lead dioxide moistened by 20 ml. of 0.175*N* caustic soda. The kerosene is filtered before and after treatment to remove suspended matter. A positive test, i.e., an increase in color, shows definite color instability of the sample, but a negative result is inconclusive. Moerbeek[180] has pointed out the desirability of using lead dioxide of standard activity. Because of the difficulty in obtaining a standard product and storing it, he recommended that lead dioxide be obtained from one source to insure at least its original uniformity. He suggested the use of the silicotungstic acid test for nitrogenous substances which might cause color instability. Van Senden[181] has proposed a somewhat different procedure in which alkaline potassium ferricyanide is used in place of alkaline lead dioxide. He found that color stability was influenced by methods of refining and storage during shipment, such as copper valves in the bottoms of tanks. The discoloration of Borneo and Rumanian gasolines is believed to be due not to nitrogenous substances but more probably to phenolic compounds or substances similar to cyclopentadiene.[182]

Lowry, Smith and Murphy[183] have developed a standardized test for color stability of gasolines. Using a commercial flame-type carbon arc as a light source (in a specially designed housing), these workers measured the change in color of various gasolines with time of exposure. Reproducible results in routine work are reported. The color instability of kerosene in storage under tropical conditions was investigated by Allibone.[184] He found that extraction with sulphur dioxide (Edeleanu process) followed by filtration through bauxite gave a product of low tint and satisfactory stability. Extraction of fuels by aqueous glycol while exposed to actinic light rays is reported to remove chromophoric substances.[185] Brooks[186] suggested the use of ammonia as a color stabilizer. Sorg[187] has investigated the power of various primary aliphatic amines, containing primary, secondary and tertiary alkyl groups, to prevent discoloration of gasoline. (See Fig. 208.) The results showed amylamine was the most satisfactory at a concentration of about 0.003 per cent. No loss of stabilizing power was observed when the amines were added to sour distillates and the latter subjected to sweetening with sodium plumbite and sulphur. The addition of a solution of pyrogallol in ethyl or isopropyl alcohol was found not only to restore the color of stored distillates but also to stabilize them satisfactorily for 6 months.[188]

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[179] E. S. Hillman, *Proc. World Petr. Congr.*, 1933, **2**, 708; *J. Inst. Pet. Tech.*, 1934, **20**, 105A; *Brit. Chem. Abs.* **B**, 1934, 742; *Chem. Abs.*, 1934, **28**, 4883.

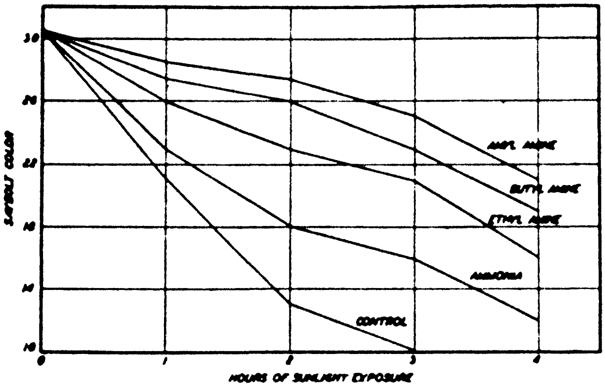
[180] B. H. Moerbeek, *Proc. World Petr. Congr.*, 1933, **2**, 713; *Brit. Chem. Abs.* **B**, 1934, 742; *J. Inst. Pet. Tech.*, 1934, **20**, 324A.

[181] G. H. van Senden, *Proc. World Petr. Congr.*, 1933, **2**, 717; *Brit. Chem. Abs.* **B**, 1934, 820.

[182] L. P. McHutton, *Proc. World. Petr. Congr.*, 1933, **2**, 721; *Brit. Chem. Abs.* **B**, 1934, 820.

[183] C. D. Lowry, Jr., M. A. Smith and G. B. Murphy, *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 140; *Chem. Abs.*, 1935, **29**, 4928; *Brit. Chem. Abs.* **B**, 1935, 614.

[184] B. C. Allibone, *Proc. World Petr. Congr.*, 1933, **2**, 725; *Brit. Chem. Abs.* **B**, 1934, 820.



Courtesy Industrial and Engineering Chemistry

FIG. 208.—Comparison of Amines as Color Stabilizers for Gasoline. (L. V. Sorg)

Many compounds which are applicable as gum inhibitors also prevent discoloration, examples of such being: urea,[189] resorcinol, pyrogallol, hydroquinone, catechol, naphthols,[190] quinhydrone[191] and cyclic organic acids such as salicylic and anthranilic,[192] primary aromatic amines,[193] unrefined corn oil[194] and aliphatic-amine salts of hydroxy-aryl compounds, e.g., hydroquinone dianilide.[195] It has been found advantageous to use polyhydroxybenzenes as color stabilizers in the presence of various gum inhibitors such as α-naphthol, α-naphthylamine or *p*-phenylenediamine[196] or an alkyl amine[197] or an anthracene or phenanthrene hydrocarbon in the presence of an α-substituted naphthalene derivative,[198] or sodium thiosulphate in the water layer (if the latter is used in storing).[199] N-Alkylated monoethanolamine has been suggested to prevent the formation of color in gasoline to which aromatic amines have been added as antioxidants.[200] Hydroxyalkylamine esters[201] and phenolates[202] have been recommended.

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[185] W. A. Schulze and F. E. Frey, U. S. P. 1,950,697, Mar. 12, 1934, to Phillips Petroleum Co.; *Chem. Abs.*, 1934, **28**, 3562.

[186] B. T. Brooks, U. S. P. 1,748,507, Feb. 25, 1930, to Gray Process Corp; *Chem. Abs.*, **1930**, **24**, 1970.

[187] L. V. Sorg, *Ind. Eng. Chem.*, 1935, **27**, 156; *Brit Chem Abs*. **B**, 1935, 888; *Chem Abs*, 1935, **29**, 6035; *Nat. Pet. News*, 1935, **27** (12), 24; *J. Inst. Pet. Tech.*, 1935, **21**, 203A.

[188] J. B. Rather and L. C. Beard, Jr., *Refiner*, 1936, **15**, 217; *J. Inst. Pet Tech.*, 1936, **22**, 356A. Also *Natl. Pet. News*, 1936, **28** (20), 34; *Chem. Abs.*, 1936, **30**, 6174; *J. Inst. Pet. Tech.*, 1936, **22**, 398A; *Oil Gas J.*, 1936, **34** (52), 209; *Chem. Abs*, 1936 **30**, 5774.

[189] J. B. Rather, L. C. Beard, Jr., and O. M. Reiff, U. S. P. 2,002,645, May 28, 1935, to Socony-Vacuum Co.; *Chem Abs.*, 1935, **29**, 4572; *Brit. Chem. Abs.* **B**, 1936, 583.

[190] J. B. Rather, O. M. Reiff and L. C Beard, Jr., U. S. P. 1,951,205, 1,951,206, 1,951,207, 1,951,208, Mar. 13, 1934, to Socony-Vacuum Co.; *Chem. Abs.*, 1934, **28**, 3579; *Brit. Chem. Abs.* **B**, 1935, 181.

[191] W. A. Smith, U. S. P. 2,003,153, May 28, 1935; *Chem. Abs.*, 1935, **29**, 4932; *Brit. Chem. Abs.* **B**, 1936, 486.

[192] French P. 785,348, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 604.

[193] T. W. Bartram, U. S. P. 2,055,810, Sept. 29, 1936, to Monsanto Chemical Co.; *Chem. Abs.*, 1936, **30**, 8599.

[194] C. D. Lowry, Jr., U. S. P. 2,014,235, Sept. 10, 1935, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1936, 917; *Chem. Abs.*, 1935, **29**, 7636.

[195] F. B. Downing and H. W. Walker, U. S. P. 2,053,466, Sept. 8, 1936, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1936, **30**, 7313.

In many cases, refining processes increase the color-stability of gasolines. For example, crude cracked gasoline may be treated with alcoholic ferric chloride before or during distillation.[203] Benedict and Wirth recommend the use at not higher than 93°C. of sulphuric acid containing ferric chloride,[204] or hydrochloric acid containing ferric sulphate.[205]

Elimination of Gum-Forming Constituents by Refining

It has been shown earlier in this chapter that the formation of gum and color in gasoline is dependent upon oxidation phenomena and may be inhibited by the addition of various substances. The latter act as antioxidants, and, during their periods of activity, prevent oxidation of unstable substances present in the gasoline. In order to conserve inhibitors occurring naturally in unrefined gasoline, Vellinger and Radulesco[206] have suggested that the unrefined distillate be distilled to give two fractions the boiling ranges of which must be determined for each fuel. The high-boiling fraction is given a mild refining treatment with clay because it contains most of the natural inhibitors. On the other hand the lighter fraction can be refined by the usual methods and then be blended with the other fraction.

Although methods of refining are beyond the scope of this book, nevertheless procedures developed primarily for the removal of unsaturated hydrocarbons which tend to yield gum are of interest and these are briefly described. They may be classified under the following general headings:

1. Clay treatment of the gasoline in either liquid or vapor phase.
2. Treatment with acids, such as sulphuric, phosphoric or hydrochloric.
3. Treatment with inorganic polymerization agents, e.g., zinc or aluminum chloride.
4. The use of alkali or alkaline earth metals and derivatives.
5. Various other reagents and treatments.

Vapor or liquid phase treatment with clay has met with some favor. Operations may be carried out using clay[207] alone or in conjunction with various substances which will effect polymerization of unsaturates. Day has described a process in which gasoline is treated with aqueous hydrogen chloride in the presence of a natural zinc-bearing clay.[208] A "gumbrin" clay also has been recommended.[209] In some cases an organic inhibitor may be added after the clay treatment.[210] Fuller's earth may form part of the bed upon which another more active inorganic substance, such as ferric sulphate, is distributed.[211]

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[196] R. E. Wilson, U. S. P. 2,023,110, Dec 3, 1935, to Gasoline Antioxidant Co.; *Chem Abs*, 1936, **30**, 850. See also R. E. Wilson and J. L. Bussies, Canadian P. 345,089, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 2350.

[197] T. H. Rogers and R. E. Wilson, U. S. P. 1,992,014, Feb. 19, 1935, to Gasoline Antioxidant Co.; *Chem. Abs*, 1935, **29**, 2349; *Brit Chem. Abs.** **B**, 1936, 87.

[198] J. L. Bussies and R. E. Wilson, Canadian P. 340,453, 1934, to the Standard Oil Co. of Ind.; *Chem. Abs.*, 1934, **28**, 3887.

[199] A metal sulphite, an acid or acid salt having a dissociation constant above 6.6 x 10^{-5} may also be used. E. N. Roberts, U. S. P. 2,050,732, Aug. 11, 1936, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1936, **30**, 6938.

[200] French P. 761,743, to Soc. anon. des carburants speciaux; *Chem. Abs.*, 1934, **28**, 4210.

[201] French P. 797,011, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 6537.

[202] W. L. Benedict, U. S. P. 2,051,814, Aug. 25, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 6938.

[203] British P. 447,533, 1936, to Carbo-Norit-Union Verwaltungs G.m.b.H.; *Brit. Chem. Abs.* **B**, 1936, 778; *Chem. Abs.*, 1936, **30**, 7313. French P. 787,929, 1935; *Chem. Abs.*, 1936, **30**, 1552.

[204] W. L. Benedict and C. Wirth, III, U. S. P. 2,013,399, Sept. 3, 1935, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1936, 917; *Chem. Abs.*, 1935, **29**, 7064.

[205] W. L. Benedict and C. Wirth, III, U. S. P. 2,013,400, Sept. 3, 1935, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1936, 917; *Chem. Abs.*, 1935, **29**, 7064

[206] E. Vellinger and G. Radulesco, *Ann. comb. liquides*, 1934, **9**, 499; *Chem. Abs.*, 1934, **28**, 6290; *J. Inst. Pet. Tech.*, 1934, **20**, 526A; *Compt. rend.*, 1933, **197**, 417; *Chem. Abs.*, 1933, **27**, 5523.

Kwal[212] has suggested the use of "Carbonit" earth and hydrogen peroxide in refining lignite spirits.

Refining may be effected in the vapor phase with a gaseous acid anhydride and steam[213] or in either the liquid or vapor phase with sulphuric[214] or phosphoric[215] acid. Treatment of distillates with hydrogen chloride, or solutions of it, in the presence of metals aids in the removal of gum-forming constituents.[216]

Inorganic polymerization agents have been employed in some of the above mentioned processes in the presence of acids, particularly hydrochloric. The use of solutions of hydrochloric acid and the chlorides of iron,[217] zinc[218] or copper,[219] or mercury[220] and solid metal oxides, as of zinc or tin at about 120°C.[221] or below a cracking temperature,[222] are examples.

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[207] French P 765,504, 1934, to Gray Process Corp.; *Chem. Abs.*, 1934, **28**, 6995. J. B. Hill, U. S. P. 2,039,904; *Chem. Abs.*, 1936, **30**, 4308. T. T. Gray, U. S. P. 1,952,751, Mar. 27, 1934; *Chem. Abs.*, 1934, **28**, 3576; *J. Inst Pet. Tech.*, 1934, **20**, 376A. T. T. Gray, U. S. P. 1,952,855, Mar. 27, 1934; *Brit. Chem. Abs* **B**, 1935, 583 *Cf.* also M. R. Mandelbaum, *Proc. World Petr. Congr.*, 1933, **2**, 21, *J. Inst Pet. Tech.*, 1934, **20**, 179A. The use of clay in refining gasoline is discussed by R. H. Price and P. I. Brandt, *Oil Gas J.*, 1935, **33** (45), 54; *J Inst. Pet. Tech.*, 1935, **21**, 260A. H. M. Steininger, *Ind. Eng. Chem*, 1934, **26**, 1039; *Chem. Abs*, 1934, **28**, 7504; *J. Inst. Pet. Tech.*, 1934, **20**, 574A; *Brit. Chem Abs.* **B**, 1935, 886 H Mainz and W. Muhlendyck, *Brennstoff-Chem*, 1934, **15**, 361, *Chem. Abs*, 1934, **28**, 7509; *J. Inst Pet. Tech*, 1934, **20**, 614A. A. F. Dudenko, *Azer. Neft. Khoz.*, **1934**, No. 6, 96; *Chem. Abs*, 1934, **28**, 5703 E. F. Engelke, U. S. P. 1,986,565, Jan. 1, 1935, to Doherty Research Co; *Brit Chem Abs.* **B**, 1935, 1083. A. A. Wells, U. S. P. 2,036,166, Mar. 31, 1936, to Standard Oil Development Co.; *Chem Abs.*, 1936, **30**, 3630; *J Inst. Pet Tech.*, 1936, **22**, 214A. E. C Herthel, U S P 1,937,759, Dec 5, 1933, to Sinclair Refining Co; *Chem. Abs*, 1934, **28**, 1179; *Brit. Chem. Abs.* **B**, 1934, 869, *J. Inst. Pet. Tech.*, 1934, **20**, 112A. J. B. Weaver, U. S. P. 1,929,861, Oct 10, 1934; *Chem Abs*, 1934, **28**, 308. *Cf.* I. Ya. Postovskii and S. P. Tzikin, *J. Applied Chem.* (*U.S.S.R.*), 1936, **9**, 61, *Brit. Chem. Abs.* **B**, 1936, 435; *Chem. Abs.*, 1936, **30**, 5756.

[208] R. B Day, U. S. P. 2,029,256, Jan. 28, 1936, to Universal Oil Products Co, *Chem. Abs*, **1936**, **30**, 1987; *J Inst. Pet. Tech.*, 1936, **22**, 158A.

[209] L. Gukhman, A. Degtyareva and A Nagiev, *Azer. Neft Khoz*, 1935, **12**, 60, *Chem. Abs.*, 1936, **30**, 8587; *J. Inst Pet. Tech.*, 1937, **23**, 20A.

[210] J. Hyman and G Ayers, Jr., U S. P. 2,039,595, May 5, 1936, to Gasoline Antioxidant Co.; *Chem. Abs.*, 1936 **30**, 4313.

[211] British P. 409,816, 1934, to Refiners Ltd and T Scott; *Brit Chem Abs* **B**, 1934, 664; *Chem. Abs.*, 1934, **28**, 6296; *J. Inst. Pet. Tech*, 1934, **20**, 425A. *Cf. Gas World*, 1935, **102**, 15; *J. Inst. Pet. Tech.*, 1935, **21**, 169A. J. C. Morrell and G. Egloff (U S. P 1,957, 794, May 8, 1934, to Universal Oil Products Co.; *Chem. Abs*, 1934, **28**, 4218; *Brit Chem. Abs.* **B**, 1935, 215) discuss the countercurrent treatment of ozone-bearing gasoline vapors with alkaline solutions in a bed of fuller's earth.

[212] B. Kwal, *Chimie et industrie*, 1936, **35**, 1040; *J. Inst. Pet. Tech*, 1936, **22**, 307A; *Brit. Chem. Abs.* **B**, 1936, 677.

[213] J. C. Morrell and G. Egloff, U. S. P 1,941,266, Dec. 26, 1933, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1934, 869. U. S. P. 1,979,565, Nov. 6, 1934; *Brit. Chem. Abs.* **B**, 1935, 892.

[214] J. C. Morrell, U. S. P. 1,941,267, to Universal Oil Products Co; *Brit. Chem. Abs.* **B**, 1934, 869. U. S. P. 1,969,316, Aug. 7, 1934; *Brit. Chem Abs.* **B**, 1935, 616 British P. 409,813, 1934, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech*, 1934 **20**, 425A; *Chem Abs*, 1934, **28**, 6297; *Brit. Chem. Abs.* **B**, 1934, 664. R. C. Osterstrom, U. S. P. 2,009,902, July 30, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 381A.

[215] G. Egloff and J. C. Morrell, U. S. P. 1,969,302, Aug. 7, 1934, to Universal Oil Products Co.; *Chem. Abs.*, 1934, **28**, 6295.

[216] R. B. Day, U. S. P. 1,937,873, Dec. 5, 1933, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**. 1934, 870; *J. Inst. Pet. Tech.*, 1934, **20**, 112A. J. C. Morrell and G. Egloff, U. S. P. 1,954,486, Oct. 4, 1934; *Brit. Chem. Abs.* **B**, 1935, 136. R. B. Day, U. S. P. 2,029,758, Feb. 4, 1936; *Chem. Abs.*, 1936, **30**, 1990; *J. Inst. Pet. Tech.*, 1936, **22**, 213A. U. S. P. 1,920,247, Aug. 1, 1933; *Chem. Abs.*, 1933, **27**, 4916; *Brit. Chem. Abs.* **B**, 1934, 440. British P. 409,901, 1934; *Brit. Chem. Abs.* **B**, 1934, 664; *J. Inst. Pet. Tech.*, 1934, **20**, 425A. German P 611,172, 1935; *Chem. Abs.*, 1935, **29**, 6041. German P. 611,339, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 220A. French P. 755,819, 1933; *Chem. Abs.*, 1934, **28**, 2174.

[217] J. C. Morrell, U. S. P. 1,988,083, Jan. 15, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 1618. See also R. B. Day, U. S. P. 2,055,027, Sept. 22, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 7835.

[218] J. C. Morrell, U. S. P. 1,988,084, Jan. 15, 1935, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 1618.

[219] G. Egloff and J. C. Morrell, U. S. P. 1,988,114, Jan. 15, 1935, to Universal Oil Products Co.; *Brit Chem. Abs.* **B**, 1935, 1126.

Treating gasoline with zinc chloride[223] polymerizes many of the gum-forming olefins present so that the stabilized gasoline may be distilled from the polymers. Other inorganic salts used similarly are aluminum chloride[224] and salts of copper,[225] iron[226] or cadmium.[227] Brückner and Lang[228] found that treatment of cracked benzine with ferric chloride results in less loss than with acid followed by alkali washing. This chloride also compared favorably with aluminum or zinc chloride as a refining agent. The addition compounds formed from aluminum chloride and olefins[229] or aluminum chloride and phenols may be used as treating agents.[230]

Operations involving the use of alkali metals have been proposed.[231] Amalgams of alkali metals,[232] the hydrides of alkaline earth or alkali metals,[233] alkali metal permanganates[234] and alkali metal pyrosulphates or persulphates with sulphuric acid[235] have been suggested for removing the gum-forming constituents of gasoline.

Other methods[236] of treating include: heating with sulphur monochloride,[237] heating,[238] hydrogenation,[239] treatment of a fraction and re-mixing,[240] treatment with copper silicate[241] followed by the addition of organic inhibitors,[242] and extraction with aqueous solutions of glycol[243] or furfural.[244] Both aryl and aliphatic sulphonic acids have been added to gasoline to resinify the polyolefins present.[245] Organic compounds containing the grouping represented by =CH—CO—, such as maleic anhydride,[246] and pyridine or hydroquinone and air in the presence of a metallic oil-soluble soap (copper naphthenate)[247] are recommended for removing gum-forming constituents from gasoline.

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[220] G. Egloff and J. C. Morrell, U. S. P. 2,057,424, Oct. 13, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 8596.

[221] J. C. Morrell and G. Egloff, U. S. P. 2,057,629, Oct. 13, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 8595.

[222] J. C. Morrell and G. Egloff, U. S. P. 2,057,630, Oct. 13, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 8595.

[223] G. Egloff, U. S. P. 1,954,867, Apr. 17, 1934, to Universal Oil Products Co.; *Chem. Abs.*, 1934, **28**, 3886, *Brit. Chem. Abs.* **B**, 1935, 136; *J. Inst. Pet. Tech.*, 1934, **20**, 426A. *Cf.* also G. Egloff, U. S. P. 2,060,291, Nov. 10, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1937, **31**, 533. A. Lachman, U. S. P. 2,042,718, June 2, 1936, to Vapor Treating Processes Inc.; *Chem. Abs.*, 1936, **30**, 5024; *J. Inst. Pet. Tech.*, 1936, **22**, 404A. The following articles are relevant: K. Musatov, *Neft. Khoz.*, 1934, **26** (2), 55, *Chem. Abs.*, 1934, **28**, 7503. D. A. Shtrom and Mil'shin *Azer. Neft. Khoz.*, **1933**, No. 4, 54; *Chem. Abs.*, 1934, **28**, 7503. *Foreign Petroleum Tech.*, 1934, **2** (9), 349; *J. Inst. Pet. Tech.*, 1935, **21**, 415A. E. Bart, Yu. Gervart and R. Baidakova *Novosti Neftepererabotki*, 1936, **3** (10), 7; *Chem. Abs.*, 1936, **30**, 6929; *J. Inst. Pet. Tech.*, 1936, **22**, 508A.

[224] A. J. van Peski, U. S. P. 2,019,772, Nov. 5, 1935, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 606. C. R. Payne and D. R. Stevens, U. S. P. 2,002,250, May 21, 1935, to Gulf Refining Co.; *Brit. Chem. Abs.* **B**, 1936, 486. A. Lachman, U. S. P. 2,035,610, Mar. 31, 1936, to Vapor Treating Processes Inc.; *J. Inst. Pet. Tech.*, 1936, **22**, 214A; *Chem. Abs.*, 1936, **30**, 3626.

[225] A. Lachman, U. S. P. 2,035,609, Mar. 31, 1936, to Vapor Treating Processes Inc.; *J. Inst. Pet. Tech.*, 1936, **22**, 214A.

[226] British P. 447,533, 1936, to Carbo-Norit Union Verwaltungs G.m.b.H.; *Brit. Chem. Abs.* **B**, 1936, 778, *Chem. Abs.*, 1936, **30**, 7313. French P. 787,929, 1935, *Chem. Abs.*, 1936, **30**, 1552.

[227] A. Lachman, U. S. P. 2,035,607 and 2,035,608, Mar. 31, 1936, to Vapor Treating Processes Inc., *Chem. Abs.*, 1936, **30**, 3626. Also uses zinc or iron salts.

[228] H. Bruckner and A. Lang, *Brennstoff-Chem.*, 1935, **16**, 126, *Chem. Abs.*, 1935, **29**, 5637.

[229] British P. 410,874, 1934; *Brit. Chem. Abs.* **B**, 1934, 790; *J. Inst. Pet. Tech.*, 1934, **20**, 458A. German P. 622,017, 1935, *Chem. Abs.*, 1936, **30**, 1553; both to I. G. Farbenind. A.-G.

[230] D. R. Stevens and W. A. Gruse, U. S. P. 2,001,634, May 14, 1935, to Gulf Refining Co.; *Brit. Chem. Abs.* **B**, 1936, 730.

[231] J. D. Fields, U. S. P. 1,983,220, Dec. 4, 1934; *Brit. Chem. Abs.* **B**, 1935, 1083. French P. 765,218, 1934, to Texaco Development Corp.; *Chem. Abs.*, 1934, **28**, 6995. J. F. Wait, British P. 441,703, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 157A; *Brit. Chem. Abs.* **B**, 1936, 260. French P. 769,117, 1934; *Chem. Abs.*, 1935, **29**, 592.

[232] E. C. Williams and H. P. A. Groll, U. S. P. 1,939,839, Dec. 19, 1933, to Shell Development Co.; *Brit. Chem. Abs.* **B**, 1934, 870.

[233] G. Egloff, U. S. P. 1,950,721, March 13, 1934, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1935, 215. See also H. V. Atwell, U. S. P. 2,042,448, June 2, 1936, to Gray Processes Corp.; *Chem. Abs.*, 1936, **30**, 5023; *J. Inst. Pet. Tech.*, 1936, **22**, 404A.

[234] J. C. Morrell, U. S. P. 2,034,197, March 17, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 3220; *J. Inst. Pet. Tech.*, 1936, **22**, 213A.

[235] J. C. Morrell, U. S. P. 1,954,487 and 1,954,488, Apr. 10, 1934, to Universal Oil Products Co.; *Brit. Chem. Abs.* **B**, 1935, 136.

[236] A. Hahn and H. Nielson, *Gas J.*, 1935, **210**, 41; *J. Inst. Pet. Tech.*, 1935, **21**, 208A.

[237] W. A. Patrick, Jr., British P. 435,194, 1935; *Brit. Chem. Abs.* **B**, 1935, 1126. French P. 770,874, 1934; *Chem. Abs.*, 1935, **29**, 919.

[238] D. R. Stevens and W. A. Gruse, U. S. P. 1,966,467, July 17, 1934, to Gulf Refining Co.; *Chem. Abs.*, 1934, **28**, 5656; *J. Inst. Pet. Tech.*, 1934, **20**, 537A. Canadian P. 324,783 and 324,785, 1932; *Chem. Abs.*, 1932, **26**, 5412. *Cf.* also Sijbren Tijmstra, U. S. P. 1,969,956, Aug. 14, 1934, to Shell Petroleum Corp.; *Chem. Abs.*, 1934, **28**, 6293; and H. Schmidt, German P. 602,034, 1934; *Chem. Abs.*, 1935, **29**, 474. D. R. Stevens and C. R. Payne, U. S. P. 2,044,739, June 16, 1936, to Gulf Oil Corp.; *Chem. Abs.*, 1936, **30**, 5781; *J. Inst. Pet. Tech.*, 1936, **22**, 404A. R. C. Osterstrom, U. S. P. 2,056,978, and 2,056,979, Oct. 13, 1936, to Pure Oil Co.; *Chem. Abs.*, 1936, **30**, 8599;

AUTOXIDATION OF LUBRICATING OILS

Fachini and Sporer[248] have classified lubricating oils into four groups:

1. Those which are unstable and sludge rapidly.
2. Those which sludge slowly at first, but afterwards more rapidly.
3. Those which sludge rapidly at first, but subsequently oxidize slowly.
4. Those which are very stable over long periods.

They aged lubricating oils artificially[249] by heating in a porcelain crucible (with specified dimensions) at 150°C. for various times. The presence of a gasoline-insoluble residue after 15, 75 or 100 hours placed the oil in Group 1, 2 or 3, respectively. Oils in which no sludge formed, even after 150 hours, were placed in Group 4.[250] According to some investigators, sludge is caused by the development of asphaltenes, and "carbon" formed by oxidation depends on the engine conditions.[251]

Gruse[252] has outlined the possible sources of coke or carbon formation as:

1. Slow oxidation of crankcase oil to resins and asphaltenes.
2. Low-temperature coking of these products in piston-ring grooves and on the piston.

J. Inst. Pet. Tech., 1937, **23**, 20A. P. F. D. Dubois, French P. 757,379, 1933; *Chem. Abs.*, 1934, **28**, 2880.

[239] D. R. Stevens and W. A. Gruse, U. S. P. 2,038,614, Apr. 28, 1936, to Gulf Oil Corp. of Pa.; *Chem. Abs.*, 1936, **30**, 4001; *J. Inst. Pet. Tech.*, 1936, **22**, 267A. *Cf.* also French P. 765,114, 1934, to International Hydrogenation Patents Co. Ltd.; *Chem. Abs.*, 1934, **28**, 6984. See also B. L. Moldavskii, V. N. Pokorskii and I. L. Andrevskii, *Neft. Khoz.*, 1935, **28**, No. 2, 52; translation in *Foreign Petroleum Tech.*, 1935, **3**, 215; *Chem. Abs.*, 1936, **30**, 3988. Carleton Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., Inc., New York, **1930**.

[240] S. M. Martin, Jr., and W. A. Gruse, U. S. P. 2,002,902, May 28, 1935, to Gulf Refining Co.; *Brit. Chem. Abs.* **B**, 1936, 486; *Chem. Abs.*, 1935, **29**, 4933.

[241] W. A. Smith, U. S. P. 1,964,087, June 26, 1934; *Brit. Chem. Abs.* **B**, 1935, 394. *Cf.* also F. J. Skowronski, U. S. P. 2,046,907, July 7, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1936, **30**, 6184.

[242] L. F. Hoyt and W. A. Smith, U. S. P. 1,975,755, Oct. 2, 1934, to W. A. Smith; *Brit. Chem. Abs.* **B**, 1935, 838; *Chem. Abs.*, 1934, **28**, 7515

[243] G. McIntyre and E. G. Ulbricht, U. S. P. 1,985,613, Dec. 25, 1934, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1935, 1128 Canadian P. 346,906, 1934, *Chem. Abs.*, 1935, **29**, 2735

[244] W. M. Stratford, U. S. P. 2,024,117, Dec. 10, 1935; *J. Inst. Pet. Tech.*, 1936, **22**, 101A.

[245] French P. 787,470, 787,471 and 787,472, 1935, to Soc. d'etudes et realisation dite Ereal; *Chem. Abs.*, 1936, **30**, 1212 See also F. R. Moser, U. S. P. 2,055,416, Sept. 22, 1936, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 7835.

[246] C. Ellis, U. S. P. 2,068,850, Jan. 26, 1937, to Standard Oil Development Co. *Cf.* also G. Stern and W. Hoess, German P. 633,346, 1936, to I. G. Farbenind. A. G.; *Chem. Abs.*, 1936, **30**, 7835.

[247] L. P. Chelbotar, U. S. P. 2,036,396, Apr. 7, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 3626; *J. Inst. Pet. Tech.*, 1936, **22**, 266A.

[248] S. Fachini and F. Sporer, *Proc. World Petr. Congr.*, 1933, **2**, 458; *J. Inst. Pet. Tech.*, 1934, **20**, 247A. *Petroleum Z.*, 1935, **31**, 23; *Motorenbetrieb*, 1935, **8** (6), 4; *J. Inst. Pet. Tech.*, 1935, **21**, 300A.

[249] The relation between artificial aging and actual service has been investigated by T. Salomon, *Chim. et ind.*, **1933**, June Special No., 562; *Chem. Abs.*, 1933, **27**, 5953. He also studied the effect of refining on stability. See also N. I. Chernozhukov and A. M. Gutzait (*Repts. Lubricating Oil Comm. U.S.S.R.*, 1933, **3**, 1; *Chem. Abs.*, 1934, **28**, 4582; *Brit. Chem. Abs.* **B**, 1935, 8) and S. J. M. Auld (*Oil Gas J.*, 1935, **34** (40), 45; *Chem. Abs.*, 1936, **30**, 3213; *J.S.C.I.*, 1936, **55**, 1014; *J. Inst. Pet. Tech.*, 1937, **23**, 72A) for the advantages of refining.

[250] S. Fachini and F. Sporer, *Giorn. chim. ind applicata*, 1933, **15**, 553; *Chem. Abs.*, 1934, **28**, 2513.

[251] D. P. Barnard, E. R. Barnard, T. H. Rogers, B. H. Shoemaker and R. E. Wilkin, *S.A.E. Journal*, 1934, **34**, 167, 181T; *Chem. Abs.*, 1934, **28**, 4584; *J. Inst. Pet. Tech.*, 1934, **20**, 524.

[252] W. A. Gruse, *Proc. World Petr. Congr.*, 1933, **2**, 441; *J. Inst. Pet. Tech.*, 1934, **20**, 246A. *Oil Gas J.*, 1933, **32** (27), 15; *Chem. Abs.*, 1934, **28**, 1166.

3. Rapid cracking of these products (and any originally present in the oil) and of unvolatilized oil on the surfaces of the combustion chamber.

Because of these three possible sources of carbon, there are three types of test which may be used in evaluating the tendency of a fuel to carbonize. These are oxidation, distillation and coking tests. Gruse believed that none of these was wholly satisfactory because oxidation tests had not established any significance for ordinary service, distillation tests did not take into account dissolved resins and coking tests did not allow for the presence of substances of excessively high boiling point.[253] Bassett[254] has suggested that coking may be ameliorated by proper choice of fuel and lubricant, filtration of air supply and the addition of an antioxidant to the lubricant.

Evers and Schmidt[255] have proposed that the aging of oils be carried out by an oxidation process. The ratio of actual increase to calculated increase in saponification number (the latter based on the amount of oxygen absorbed) is about 1 :3 for oils. This is said to show the formation of oxygen compounds other than acids or esters. These investigators proposed that the rate of absorption of oxygen by an oil be determined under specified conditions and be used as an index of the oxidizability of the oil. They recommended absorbing the oil on silica gel impregnated with cupric oxide and oxidizing it with pure oxygen at 100°C. and atmospheric pressure. The rate of absorption was followed by measuring the current necessary to form enough oxygen by electrolysis so that the pressure in the reaction chamber remained constant. The whole operation is carried out in a specially designed apparatus and is reported to be quick and accurate, and the results are said to be reproducible.

Using the method of Evers and Schmidt, Lederer[256] has studied the rate of oxidation of hydrocarbons, alcohols, phenols, aldehydes, fatty acids and benzene. He found that there was evidence of peroxide formation in the oxidation of compounds containing not less than two double bonds and an active group such as hydroxyl or carboxyl. He reported that the "oxidation number"[257] is generally sufficient to give insight into the oxidation characteristics of lubricating and transformer oils. Chernozhukov[258] investigated the oxidizability of several Russian and other lubricating oils. He employed the Butkov[259] method for the oxidation at 150°C. and 15 atmospheres of oxygen.

Evans studied the oxidation of lubricating oils by heating in a sealed glass tube, rotated so that a new film of oil would always be exposed.[260] He stated that at certain temperatures the oil molecule is broken down into substances which tend to cause sticking of the piston-rings and carbonization.[261] The oxidation-stability of oil for use in aeroplane engines was found to be of greater importance than its oiliness. Oxidation was catalyzed by various metallic substances. The composition of the sediment is the same whether formed in laboratory or in an engine, but a highly oxidized form is found in the hotter portions of the motor.[262]

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[253] In this connection, see J. Formanek, *Automobiltechn. Z.*, 1934, **37**, 398; *Brennstoff-Chem.*, 1934, **15**, 433; *Chem. Abs.*, 1935, **29**, 915. *Chem. Obzor.*, 1933, **8**, 169, 189; *Chem. Abs.*, 1934, **28**, 4892.

[254] H. N. Bassett, *Gas & Oil Power*, 1934, **29** (344), 138; *J. Inst. Pet. Tech.*, 1934, **20**, 429A.

[255] F. Evers and R. Schmidt, *Proc. World Petr. Congr.*, 1933, **2**, 444; *Brit. Chem. Abs.* **B**, 1934, 742; *J. Inst. Pet. Tech.*, 1934, **20**, 315A.

[256] E. L. Lederer, *Petroleum Z.*, 1935, **31** (44), 1; *Chem. Abs.*, 1936, **30**, 2734.

[257] See F. Evers and R. Schmidt, *loc. cit.*

[258] N. I. Chernozhukov, *Repts. Lubricating Oil Comm. U.S.S.R.*, 1933, **3**, 23; *Chem. Abs.*, 1934, **28**, 4582; *Brit. Chem. Abs.* **B**, 1935, 8. For the lubricating-oil fractions from several Russian oils, see also A. S. Velikovskii and A. V. Vasil'eva, *Neft. Khoz.*, 1935, **29** (9), 62; *Foreign Petroleum Tech.*, 1936, **4**, 209; *Chem. Abs.*, 1936, **30**, 8590.

[259] For the methods of N. A. Butkov, see Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., New York, 1934.

[260] E. A. Evans, *Proc. World Petr. Congr.*, 1933, **2**, 460; *J. Inst. Pet. Tech.*, 1934, **20**, 85A; *Brit. Chem. Abs.* **B**, 1934, 997.

[261] *Cf.* also the work of T. Salomon, *Ann. combustibles liquides*, 1930, **5**, 831; *Chem. Abs.*, 1931, **25**, 4392.

Garner and his co-workers[263] have studied the influence of various factors, such as contaminations and temperature variations, on the results obtained in the British Air Ministry test. This test consists of the passage of 15 liters of air an hour through a 40 cc. sample of oil maintained at 200°C. for 2 periods of 6 hours each on consecutive days. After this treatment, the stability of the oil is determined by the changes produced in the coke number and the viscosity. Auld[264] has suggested that the test may be made a little more discriminating by raising the temperature to 250°C. Comparison of the British test with that of the French Air Ministry has shown similarity of results with these two methods.[265] Although the absolute values of six various types of oils differed with the test employed, there was the same order of classification in each case. The fact that the British and French tests employ different methods (the former carried out at 200°C. without a catalyst and the latter at 140°C. with a catalyst), and yet classify lubricating oils in the same order, was taken to confirm the view that deterioration takes place by oxidation and polymerization and that a catalyst such as copper accelerates but does not change the nature of the reaction.

Heating lubricating oils at 130°C. for 50 hours in the presence of air and of copper has been suggested as an aging test by Dackweiler.[266] The results parallel those for the measurement of ether-insoluble asphalts. Chernozhukov and Krein[267] have studied the oxidation of lubricating oils containing naphthenes and aryl and hydroaryl hydrocarbons. They found that a lubricating oil composed of naphthenes and 15 to 20 per cent aromatic hydrocarbons increased in acidity on oxidation but formed no precipitate. The course of the reaction followed was that which it would have taken in the absence of naphthenes. However, in the presence of 10 per cent or less of aromatics, the oxidation followed the course for straight naphthenes. They also observed that if there was 5 per cent of hydroaryl hydrocarbons in a naphthenic oil, a precipitate was formed on oxidation which consisted of hydroxy-acids, asphaltenes and carbenes. At higher concentrations the hydroxy-acids are the predominant products. The asphaltenes were thought to originate from the aralkyl hydrocarbons, such as diphenylmethane and its homologues, which may occur in the oil.

In Diesel engines, aging of lubricating oils is said to consist in an oxidation which takes place on the cylinder walls, resulting in the formation of asphaltic products. The latter are insoluble in the oil but soluble in chloroform.[267a] Further aging leads to products insoluble even in chloroform.

Dornte and Ferguson[268] investigated the oxidation of oils whose oxidation is unaffected by the non-volatile products formed. They showed that the total oxygen absorbed was a linear function of the time at constant oxygen pressure and constant temperature. Water and carbon dioxide, with some carbon monoxide, were the only products of oxidation. The absence of peroxides was believed to be characteristic of this type of reaction. The catalytic powers of copper, iron, lead and tin were studied. Copper had a rather pronounced effect, while the others exerted little if any influence. The metal to oil ratio and partial pressure of the oxygen affected the catalytic power, especially of copper. Similar work subsequently was undertaken with that type of lubricating oil whose rate of oxygen absorption continuously decreases, probably due to a decreasing concentration of the reacting components of the oil.[269] From the oxygen absorption data, an empirical equation was obtained:

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[262] J. Damian, *Compt. rend. Congr. Graissage*, **1931**, 286; *Brit. Chem. Abs.* **B**, 1933, 376; *Chem. Zentr.*, 1932, **2**, 2571.

[263] F. H. Garner, C. I. Kelly and J. L. Taylor, *Proc. World Petr. Congr.*, 1933, **2**, 448; *Brit. Chem. Abs.* **B**, 1934, 997.

[264] S. J. M. Auld, *J. Inst. Pet. Tech.*, 1936, **22**, 57; *Brit. Chem. Abs.* **B**, 1936, 308.

[265] J. Damian and R. Jeannin, *15me Congr. chim. ind.* (Bruxelles, Sept. 1935), **1936**, 492; *Chem. Abs.*, 1936, **30**, 5776.

[266] H. Dackweiler, *Bull. soc. belge elec.*, 1933, **49**, 550; *Chem. Abs.*, 1934, **28**, 4892.

[267] N. I. Chernozhukov and S. E. Krein, *J. Appl. Chem. Russ.*, 1935, **8**, 251; *Brit. Chem. Abs.* **B**, 1935, 711.

[267a] A. Acker and F. Rengade, *Ann. combustibles liquides*, 1936, 11, 945; *Chem. Abs.*, 1937, **31**, 1189.

[268] R. W. Dornte and C. V. Ferguson, *Ind. Eng. Chem.*, 1936, **28**, 863; *J. Inst. Pet. Tech.*, 1936, **22**, 357A.

$$V^2 = kt$$

where V = total volume of oxygen absorbed in cc. at standard conditions per 100 grams of oil,
t = time in hours,
and k = rate constant obtained by plotting V^2 against t.

This equation indicates that the reaction probably was retarded by the oxidation products. However, the rate of reaction varied linearly with the partial pressure of the oxygen. In addition to the oxidation products of the first type of oil,[270] acids were detected and similar catalytic effects of metals were noted. Below 250°C. tin and some of its compounds act as antioxidants for lubricating oils.[271] The extent of this effect depends upon the specific compound, the type of oil, concentration in the oil and other conditions of the test. Soluble fatty acid salts, naphthenates, phenolates and such organo-metallic derivatives as tin tetraphenyl were found to be oxidation inhibitors. It was suggested that the tin compounds might have reacted with an auto-catalyst formed during oxidation. Tin tetraethyl and tin ricinoleate may be used in amounts up to 1 per cent.[272]

Various investigators have suggested tests to ascertain the stability of oils to oxidation.[273] Guthrie and co-workers[274] have proposed a "stability number" which is said to be useful in conjunction with results obtained in service. The procedure is to oxidize 150 cc. of oil for 5 hours at 388.8°F. by passing 2.2 liters of oxygen through it per hour. The changes produced in kinematic viscosity, carbon residue, precipitation number and neutralization number are determined. The "stability number" is then one-fourth of the sum of 4 times the change in viscosity, plus 100 times the change in carbon residue and 100 times the changes in both the precipitation number and neutralization number.

Rogers and Shoemaker[275] have described the widely used Indiana Oxidation test. This is carried out in oil test tubes, 40 to 44 mm. inside diameter and 450 to 500 mm. in length, and placed in an oil bath heated to approximately 342°F. The apparatus is shown in Fig. 200. The temperature can be regulated closely by means of electric heating units. Air is blown through the oil samples at a predetermined rate. At intervals samples are taken and asphalts determined by precipitation with naphtha. The times required for the formation of 10 and 100 mg. of asphaltene per 10 g. of oil are determined as indexes of the oxidizability of the oil. Details of the procedure are:

> "Fill the oil tube to a depth of 23 cm. (approximately 300 cc. of oil). Place the tube in the bath, the level of which must be at least 5 cm. above that of the test oil. The oil bath must be up to temperature and so maintained that the temperature of the

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[269] R. W. Dornte, C. V. Ferguson and C. P. Haskins, *Ind. Eng. Chem*, 1936, **28**, 1342; *Chem. Abs.*, 1936, **30**, 8591; *J. Inst. Pet. Tech.*, 1937, **23**, 29A.

[270] R. W. Dornte and C. V. Ferguson, *loc. cit.*

[271] E. W. J. Mardles, *Chem. Trade J.*, 1934, **95**, 256; *J. Inst. Pet. Tech.*, 1935, **21**, 61A.

[272] P. C. Barbosa, *Rev. chim. ind.* (Rio de Janeiro), **1935**, 404; *Chem. Abs.*, 1936, **30**, 1217.

[273] For a discussion of oxidation tests the reader may consult Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, **1934**. Also E. P. Redgrove, *Petroleum Times*, 1934, **32**, 583; *Chem. Abs.*, 1935, **29**, 4565. *Cf.* British P. 421,226, 1934, to "Yacco" S.A.F.; *Brit. Chem. Abs.* **B**, 1935, 136; *J. Inst. Pet. Tech.*, 1935, **21**, 100A.

[274] B. Guthrie, R. Higgins and D. Morgan, *Nat. Pet. News*, 1934, **26** (32), *22*; **26** (33), *22*; *J. Inst. Pet. Tech.*, 1934, **20**, 568A.

[275] T. H. Rogers and B. H. Shoemaker, *Ind. Eng. Chem.*, *Anal. Ed.*, 1934, **6**, 419; *Brit. Chem. Abs.* **B**, 1934, 54; *Chem. Abs.*, 1935, **29**, 1236

test oil is 341 ± 0.5°F. The air delivery tube is placed so that the end is within 6 mm. of the bottom of the oil tube. One-half hour after placing the oil in the bath, start the air at a rate of 10 ± 1 liters per hour (as measured under laboratory conditions). The start of the test period is the time of starting the air.

"For determination of the sludge values withdraw a 25-cc. sample of the test oil in a pipet. Weigh 10 grams (± 0.1 g.) of this portion immediately into a 300-cc. Erlenmeyer flask, and dilute with 100 cc. of A.S.T.M. precipitation naphtha.[78] The naphtha used must, by comparative test on a sample of oxidized oil, give within 25 per cent of the sludge value obtained with a reference sample of A.S.T.M. precipitation naphtha. Stopper the flask and allow the solution to stand for 3 to 3.5 hours at room temperature (70 to 85°F., 21.1 to 29.4°C.).

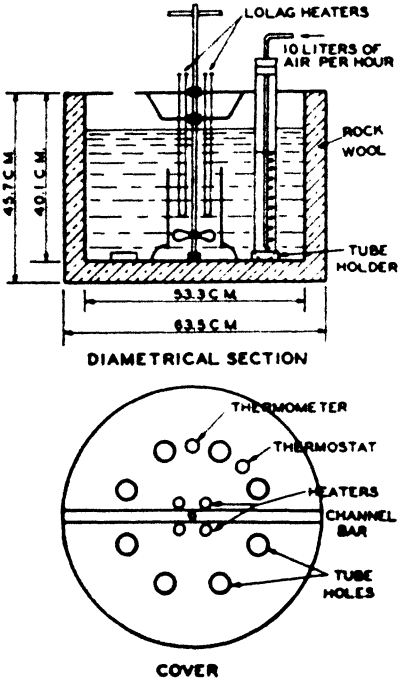

FIG. 209.
Drawing of Apparatus for Indiana Oxidation Test. (T. H. Rogers and B. H. Shoemaker)

Courtesy Industrial and Engineering Chemistry

"Prepare a Gooch type crucible (approximately 35 mm. in diameter) with a mat of 0.5 to 0.65 g. of medium asbestos fiber. During preparation of the mat, press it down before adding the last portion. Dry the crucible at approximately 300°F. (148.9°C.) for at least 2 hours in an oven and weigh. Filter the sample, wash with precipitation naphtha, heat at approximately 300°F. for 0.5 hour and weigh. Express the sludge as milligrams per 10 g. of oil."

"Samples for sludge determinations may be taken every 24 hours before sludging begins. Take at least three samples giving sludge values between 5 and 125 mg., including one between 5 and 20 and one between 50 and 125. A plot of these values *vs.* time on log paper is then used to determine the sludging time and the 100 mg. time. For tests made at barometric pressures differing by more than 5 per cent from 1 atmosphere, correct these times to normal barometric pressure by multiplying the observed time by the ratio of the barometric pressure during the test to 760.

"For determination of viscosity increase, samples of approximately 75 cc. are withdrawn every 50 hours and used to run Saybolt viscosity. This oil is then replaced in the test tube."

This test is said to be reproducible within 10 per cent by different operators.

[78] *Am. Soc. Testing Materials*, Section 6 (a), Method D91-33, *A.S.T.M. Standards*, Part II, 1933.

Fairlie[277] has designed an apparatus in which oil may be aged to give results comparable to actual use in a motor. The apparatus consists of a sump from which oil is pumped into a header-tank. From this it flows to an aerator and then through a heating coil 40 feet long. It passes from the heater to a cooler in which the cooling water runs at a rather high temperature (at boiling if room temperature is above 80°F.). The essential conditions are: 4 liters of oil in sump, 220°F. sump temperature, 300 ml. per hour flow through heater and a heater outlet temperature of 425°F. Tests are run for 150 hours, samples being taken at the end of 50, 100 and 125 hours and inspected for the proportion of sediment or sludge formed.

The experimental study of the oxidation of lubricating and heavier oils has shown, according to Obenaus,[278] that reliance upon the results of only one test, such as carbon residue, acid number or viscosity, may give erroneous conclusions as to the aging properties of the sample. According to Nikiforov and his collaborators, oxidation of motor oils by various methods showed that the main change was cracking due to the action of metals at high temperatures on the oil.[279]

By treating transformer oil sludge with dilute aqueous nitric acid and ether, Boisselet and Mouratoff[280] found that the oxidation products included acids and metallic soaps. Extraction of either used or aged motor oil with sodium hydroxide has given various oxy-acids.[281] The extraction of an alkali-treated oil with gasoline removes resinous material[282] and hence influences the tar number as determined by the Kissling test.[283]

Water vapor has so pronounced an influence on asphalt formation that even the humidity of the laboratory may affect the amount precipitated from aged mineral oils by benzine.[284] Organic substances, such as acetone and alcohol, also increase the amount of precipitate. Consequently precipitations should be carried out in tight containers where contaminants can not be introduced, and the solutions should settle in the dark. Weiss and Vellinger[285] have studied the oxidation of oil and found that increased water vapor decreased the amount of deposit and increased the volatile acids formed as shown in Fig. 210. They considered that the study of several properties, such as sludge formation, fixed and volatile acidity, interfacial tension, and color during artificial aging of any class of oil, showed more in regard to the properties of that oil than the volume of oxygen absorbed.

Investigations have shown that oiliness decreases quite rapidly by oxidation at 75°C.[286] Substances such as β-naphthol act as inhibitors for the reaction and simultaneously improve the lubricating properties of the oil to a certain extent. King[287] has investigated the behavior of oils under relatively high temperatures (200 to 300°C.) and found that oils which normally maintain a film up to 160°C.

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[277] M. Fairlie, *Oil Gas J.*, 1935, **33** (45), 58; *J. Inst. Pet. Tech.*, 1935, **21**, 255A; *Chem. Abs.*, 1935, **29**, 4560.

[278] W. Obenaus, *Angew. Chem.*, 1935, **48**, 587; *Brit. Chem. Abs.* **B**, 1935, 1032.

[279] L. Nikiforov, M. Vorenko, S. Beider, N. D. Gramenitzkii, M. M. Fainger, V. P. Nikol'skaya, I. Iz. Ignatovskaya and E. A. Vlasova, *Neft. Khoz.*, 1934, **26** (4), 44; *Chem. Abs.*, 1934, **28**, 7496; *Brit. Chem. Abs.* **B**, 1935, 392.

[280] L. Boisselet and C. Mouratoff, *Ann. comb. liquides*, 1934, **19**, 69; *Chem. Abs.*, 1934, **28**, 3881; *J. Inst. Pet. Tech.*, 1934, **20**, 315A

[281] H. Müller, and W. Müller, *Petroleum Z.*, 1934, **30**, (45); *Montan. Rudschau*, 1934, **26**, No. 23, 5; *Motorenbetrieb*, 1934, 7, 5; *Chem. Abs.*, 1935, **29**, 2722; *Brit. Chem. Abs.* **B**, 1935, 8; *J. Inst. Pet. Tech.*, 1935, **21**, 17A.

[282] K. Weisselberg, *Petroleum Z.*, 1934, **30**, No. 4, 5; *Chem. Abs.*, 1934, **28**, 3881; *J. Inst. Pet. Tech.*, 1934, **20**, 165A; *Brit. Chem. Abs.* **B**, 1934, 308.

[283] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

[284] A. Maillard and M. A. Acker, *14me Congr. Chim. ind. Paris*, Oct., 1934; *Ann. comb. liquides*, 1935, **10**, 465; *Chem. Abs.*, 1935, **29**, 6749; *J. Inst. Pet. Tech.*, 1935, **21**, 374A.

[285] H. Weiss and E. Vellinger, *Proc. World Petr. Congr.*, 1933, **2**, 423; *J. Inst. Pet. Tech.*, 1934, **20**, 315A; *Brit. Chem. Abs.* **B**, 1934, 742.

[286] F. H. Rhodes and A. W. Lewis, *Ind. Eng. Chem.*, 1934, **26**, 1011.

[287] R. O. King, *J. Inst. Pet. Tech.*, 1934, **20**, 97; *Chem. Abs.*, 1934, **28**, 3572; *Brit. Chem. Abs.* **B**, 1934, 309; *J. Inst. Pet. Tech.*, 1934, **20**, 260A. For details and a discussion of the results, the original paper should be consulted.

could lubricate up to 300°C. because of what he termed "oxidation lubrication." This was observed, for example, in the case of a blend of 40 per cent "bright stock" and 30 per cent each of a paraffin and asphaltic base distillate.

OXIDATION OF WHITE OILS

The oxidation of white oils is a rather special example of the oxidation of lubricating oils which are prepared by drastic refining. Dornte[288] reported that the oxidation of white oil is an autocatalytic process involving a chain mechanism. He deduced an empirical equation to represent the results of his experiment:

$$V^{\frac{1}{2}} = kt + n$$

in which V is the volume of oxygen absorbed in cubic centimeters reduced to standard conditions per 100 g. of oil, k is the constant which characterizes the rate of oxidation reaction, t is the time in hours and n is considered a function of inhibition due to natural inhibitors present. It is negative when an inhibitor such as phenyl-α-naphthylamine has been added. Experiments were conducted by the absorption of oxygen at 115 to 145°C.

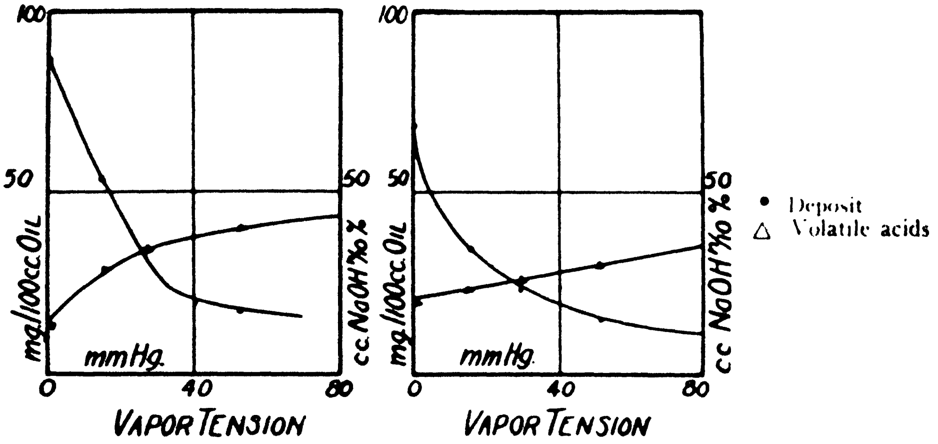

FIG. 210.—Influence of Air Humidity on Oxidation Products from Two Oils. (H. Weiss and E. Vellinger)

The oxidation of synthetic mixtures of naphthenic hydrocarbons (pure medicinal white oils) and aromatic hydrocarbons by the method of Butkov[289] has shown that aromatic compounds in general are more readily oxidized than naphthenic hydrocarbons, although the latter seem to induce the reaction.[290] The antioxidant properties of aromatic substances are improved by the presence of a trivalent carbon or an increase in the number of rings. Inhibitors of the oxidation of naphthenes are phenols, quinones and resins of aromatic origin, although they affect the appearance of the oils.[291] On the other hand, aldehydes, ketones, acids, hydroxy acids and phenol acids reduce their stability.

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[288] R. W. Dornte, *Ind. Eng. Chem.*, 1936, **28**, 26; *Brit. Chem. Abs.* B, 1936, 307; *Chem. Abs.*, 1936, **30**, 1215.

[289] N. A. Butkov, *Neft. Khoz.*, 1927, **13**, 332; *Chem. Abs.*, 1928, **22**, 2458.

[290] N. I. Chernozhukov and S. E. Krein, *Neft. Khoz.*, 1933, **25**, 35, 102; *Chem. Abs.*, 1934, **28**, 621.

Yamada[292] has observed that a greater proportion of acidic substances is formed in the oxidation of white oil in the absence of dehydrating agents, such as phosphorus pentoxide or potassium hydroxide, than in their presence. This is analogous to the results reported by Weiss and Vellinger[293] on the action of water. Alcohols were found to be primary oxidation products although they were not active centers for subsequent oxidation.

The stabilization of white oils is effected in the same way as in the case of other petroleum products, viz., by the addition of antioxidants. Alkene diamines of the types $H_2N\text{-}CHR\text{-}CHR'\text{-}NH_2$ and $(CH_2)_n(NH_2)_2$ or their derivatives,[294] oil soluble mercaptans containing more than 7 carbon atoms,[295] and aromatic mercaptans or disulphides or the corresponding selenium or tellurium compounds[296] are useful as antioxidants for refined petroleum oils. Archibald[297] has noted that refining of mineral oil to give a product to conform to the U. S. Pharmacopoeia removes some substances which are antioxidants. He has suggested ether-extraction of the clay used in filtering the oil, distilling off the solvent and adding small amounts (0.02 to 1.0 per cent) of the residual oil to the final product to protect the latter against oxidation. The methyl alcohol-extract of spindle oil may be blended with a highly refined white oil to give an insulating oil.[298]

OXIDATION INHIBITORS FOR LUBRICATING OILS

The formation of sludge by the autoxidation of lubricating oils has been investigated by Tanaka, Kobayashi and Furihata.[299] They reported that substances which acted as antioxidants under certain conditions might be pro-oxidants in oils with other characteristics. They proposed an explanation based on the formation of a peroxide of the autoxidizable substance, A, which can react with the added substance, B:

$$A\,O_2 + B \underset{K_2}{\overset{K_1}{\rightleftharpoons}} B\,O_2 + A$$

where K_1 and K_2 are the reaction-velocity constants in the directions indicated. The higher the ratio of K_1 to K_2, the more effective B is as an antioxidant

The autoxidation of lubricating oils in storage may be hindered by methods similar to those used for gasolines and white oils. White lubricating oils may be blended with pale lubricating oils to stabilize the latter[300] against sludge formation. Shoemaker[301] has suggested the addition of an oil-soluble amide such as dibutyl sodamide. The naphthenates of various metals, such as manganese, lead, zinc, copper, aluminum, cobalt or calcium, are stabilizers for lubricating and transformer oils.[302] Tin compounds, such as tin oleate and tin tetraphenyl, are reported to inhibit the deterioration of oils,[303] whereas compounds of copper, iron, silver, vanadium and manganese are said to accelerate the rate of deterioration. Compounds of gold, mercury, chromium, cerium, bismuth and antimony have little influence. Tin compounds may be added with lead compounds, the latter intended to raise the spontaneous ignition temperature.[304] Chromium oleate is reported to inhibit oxidation and minimize the corrosion of metal surfaces.[305] Organic compounds of tin or lead may be added together with an oil-soluble organic compound of chromium.[306] Organic derivatives of elements of Groups II, III or V of the Periodic Table may be added to lubricating oils.[307] Examples are trinaphthyl-α-propyl bismuthine, cadmium dicresyl, triphenyl bismuth and di-tolyl mercury. They are said to be effective at 200-250°C. Aromatic disulphides and mercaptans and the corresponding selenium and tellurium compounds are reported to be inhibitors in oils, other than white oils, which have a high rate of oxidation.[308] Hydroxy- and amino-diaryl ethers or sulphides have been suggested as antioxidants.[309]

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[291] N. I. Chernozhukov and S. E. Krein, *Neft. Khoz.*, 1935, **28** (3), 59; *Foreign Petroleum Tech.*, 1935, **3**, 577; *Chem. Abs.*, 1936, **30**, 2356.

[292] T. Yamada, *J. Soc. Chem. Ind. Japan*, 1931, **34**, Suppl. binding, 493; 1932, **35**, Suppl. binding, 202, 467; *Chem. Abs.*, 1932, **26**, 3366, 4703; 1933, **27**, 1493.

[293] H. Weiss and E. Vellinger, *loc. cit.*

[294] V. Voorhees, Canadian P. 351,723, 1935, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 6751.

[295] R. G. Sloane, U. S. P. 1,966,050, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1935, 485; *Chem. Abs.*, 1934, **28**, 5653.

[296] R. G. Sloane, Canadian P. 356,175, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 2749.

[297] F. M. Archibald, U. S. P. 2,035,418, Mar. 24, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 3168; *J. Inst. Pet. Tech.*, 1936, **22**, 216A.

[298] K. Typke, *Erdöl u. Teer*, 1933, **9**, 29, *Chem. Zentr.*, 1933, **1**, 2202; *Chem. Abs.*, 1934, **28**, 5651.

[299] Y. Tanaka, R. Kobayashi and M. Furihata, *J. Soc. Chem. Ind. Japan*, 1935, **38**, *suppl. binding*, 417; *Chem. Abs.*, 1935, **29**, 8301; *Brit. Chem. Abs.* **B**, 1935, 1032.

[300] A. E. Becker and W. S. Davis, U. S. P. 1,966,111, July 10, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1934, **28**, 5658; *J. Inst. Pet. Tech.*, 1934, **20**, 540A.

[301] B. H. Shoemaker, U. S. P. 2,012,918, Aug. 27, 1935, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 7064.

The mechanism of the oxidation of transformer oils is very similar to that for lubricating oils.[310] Vellinger and Müller[311] have investigated the oxidation of mineral oils by atmospheric oxygen at temperatures between 100 and 150°C. In the accompanying graphs, Fig. 211, the effect of addition of copper stearate in amounts of 2 to 25 mg. to 100 cc. of oil is shown.

In experiments in which copper stearate was added directly to the oil, curves such as *A* were obtained. Curve A_1 represents a mixture containing 25 mg. copper stearate per 100 cc. of oil, A_2 containing 10 mg., A_3 5 mg., and A_4 2 mg. However, it will be noticed that in curve *B* the initial period (from its origin to point *T*) influences the rate of asphalt formation. During this period copper was being dissolved from small, polished copper cubes placed in the oil. After the time *T*, even removing the cubes entirely had no effect because they had become inactivated by adsorption of some substance present in the oil and did not dissolve any further. When the oil was initially acid either from an added organic acid or from heating in the absence of a metal, copper dissolved very readily and a curve such as *C* was obtained.

From these results Vellinger and Müller concluded that the rate of formation of sludge in a transformer oil depends upon the amount of dissolved copper. The area of copper exposed to the oil had an influence on the amount of asphalt formed (Curve *D*) because of the greater amount of copper dissolved from a large surface. Curve *E* shows the effect of copper stearate on the reaction velocity of the oxidation.

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[302] C. K. Parker, U. S. P. 2,001,108, May 14, 1935, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1935, **29**, 4570; *Brit. Chem. Abs.* **B**, 1936, 630.

[303] E. W. J. Mardles, *Tech. Pub. Intern. Tin Research and Development Council C* 1934, No 2; *Chem. Abs.*, 1935, **29**, 3504; *Brit. Chem. Abs.* **B**, 1934, 997 *Cf.* also H Suida and P. Franchetti, *Petroleum Z.*, 1935, **31**, No. 49; *Motorenbetrieb u. Maschinen-Schmierung*, 1935, **8**, No. 12, 2; *Chem. Abs.*, 1936, **30**, 3213; *J. Inst. Pet. Tech.*, 1936, **22**, 56A.

[304] W. Helmore and E. W. J. Mardles, British P. 398,222, 1933; *Chem. Abs.*, 1933, **27**, 1525.

[305] A. A. Griffith and W. Helmore, British P. 423,441, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 175A; *Brit. Chem. Abs.* **B**, 1935, 346.

[306] British P. 431,066, 1933, to C. C. Wakefield & Co. Ltd.; *Brit. Chem. Abs.* **B**, 1935, 760. Austrian P. 141,869, 1933; *J. Inst. Pet. Tech.*, 1935, **21**, 312A.

[307] British P. 433,257, 1935, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1935, 937; *J. Inst. Pet. Tech.*, 1935, **21**, 423A. French P. 789,595, 1935; *Chem. Abs.*, 1936, **30**, 1992.

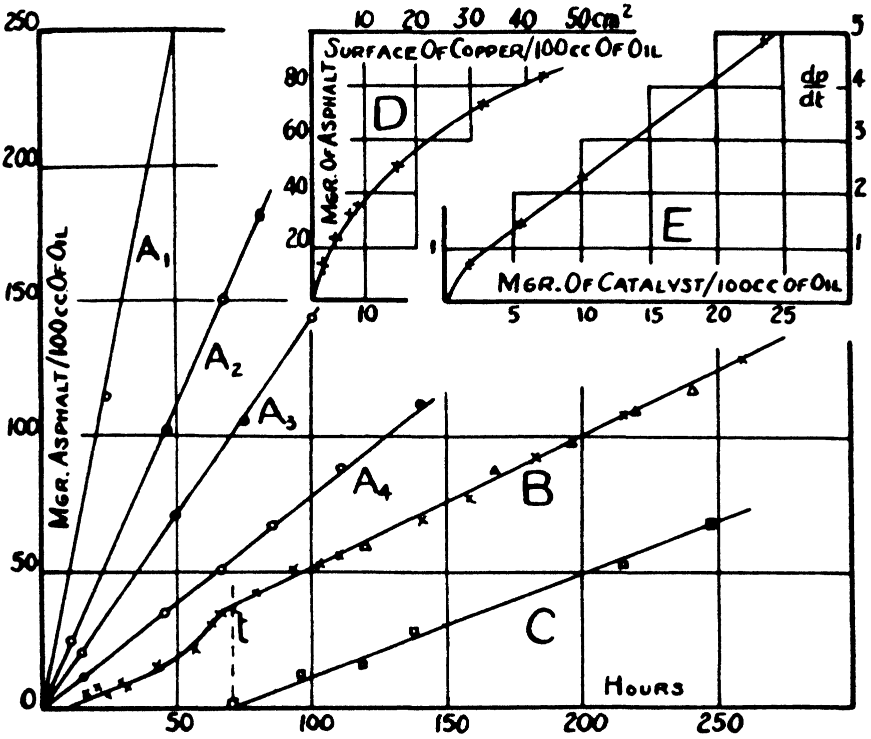
[308] British P. 425,569, 1935, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1935, 441; *Chem. Abs.*, 1935, **29**, 5650.

[309] British P. 442,161, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 3822; *Brit. Chem. Abs.* **B**, 1936, 439. *Cf.* also R. Rosen, Canadian P. 356,177, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 2748.

[310] A study of the oxidation of crude oils has shown that certain changes may be expected: 1. Formation of CO_2; 2. Formation of asphaltic and gummy substances; 3. Increase in acidity: 4. Unchanged surface tension; 5. Decrease in interfacial tension. S. S. Taylor and H. M. Smith, *Bur. Mines, Rept. of Investigations*, 1934, 3238.

[311] E. Vellinger and G. Müller, *Compt. rend.*, 1934, **198**, 2252; *Chem. Abs.*, 1934, **28**, 5643. See also H. Schwarz, *Petroleum Z.*, 1935, **31**, 7. *Cf.* G. Müller, *Compt. rend.*, 1935, **200**, 1769; *Brit. Chem. Abs.* **B**, 1935, 709. Müller has studied the oxidation of transformer oil on prolonged heating. He found no relation between the volume of oxygen absorbed and the formation of deposit.

Gemant[312] has measured the absorption of air by mineral oil at 20 and 80°C. He concluded from his data that the absorption is not purely physical but is accompanied by a reversible oxidation. It has been observed that the oxidation of transformer oil is a monomolecular reaction in which the reaction constants and energy of activation vary because of the presence of different hydrocarbons.[313] It was also reported that activation energy increased with the time of oxidation because of the disappearance of readily oxidizable material and not because of autocatalysis. Oxidation of over-refined oils gave products which remained in solution, although the reverse occurred with under-refined oils.



Courtesy Librairie Imprimerie Gauthier Villars

FIG. 211.—Effect of Copper Stearate on Rate of Asphalt Formation in Air Oxidation of Mineral Oils. (E. Vellinger and G. Muller)

Thin films of tin, lead and copper have a catalytic effect on the formation of sludge in insulating oils, which increases in the order named. The effect of tin, however, is slight, and it may even be an anti-oxidant.[314] Copper catalyzes the oxidation of naphthenes to asphaltogens more readily than iron, although the activity is reversed in the oxidation of aromatic hydrocarbons to phenols.[315] Kurlin and Blinova,[316] among others, have observed that severe refining decreases the stability of oils. Over-refined oils have been used in transformers in order that the inert gas formed by their decomposition may remain above the oil and reduce explosion hazards.[317] Contrary to beliefs once held, the addition of fresh oil to a transformer does not increase the rate of sludge formation unless, in some cases, the original oil was of inferior quality or excessively aged.[318]

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[312] A. Gemant, *Trans. Faraday Soc.*, 1936, **32**, 694; *J. Inst. Pet. Tech.*, 1936, **22**, 252A; *Brit. Chem. Abs.* **B**, 1936, 435; *Chem. Abs.*, 1936, **30**, 4656. *Trans. Faraday Soc.*, 1936, **32**, 1628; *Chem. Abs.*, 1937, **31**, 842.

[313] L. S. Ornstein, C. Janssen, Sr., C. Krijgsman and D. Th. J. ter Horst, *Physica*, 1935, **2**, 201; *J. Arch. Elektrot.*, 1930, **25**, 567; 1933, **27**, 489; *Chem. Abs.*, 1935, **29**, 7060; *Brit. Chem. Abs.* **B**, 1935, 484.

[314] P. J. Haringhuizen and D. A. Was, *Proc. K. Akad. Wetensch. Amsterdam*, 1935, **38**, 1002; *Brit. Chem. Abs.* **B**, 1936, 134; *J. Inst. Pet. Tech.*, 1936, **22**, 102A.

The effect of circuit-breaking and high temperatures on a transformer oil has been studied,[319] and it was found that the amount of gas formed increased rather rapidly with the number of breaks and came out of solution readily.

One of the most important properties desired in a transformer oil is resistance to that oxidation[320] which results in the formation of sludge and acid.[321] This is a sequence of unimolecular reactions of the different oils present. Weiss and Salomon[322] have used the time required for the production of a trace of deposit in oil heated at 114-117°C. in contact with air as an index of alterability. They classified oils which formed deposits in less than 10 hours as very alterable. Those yielding deposits of more or less than 0.008 g. (per 100 cc.) in 15 to 24 hours were considered to be of average and slight alterability, respectively. If the time required for deposition was longer than 36 hours the oil was very slightly alterable. Gemant[323] described a rapid measurement of the oxidation of insulating oils in air. In his method, a sample of oil is kept in a closed space at 145 or 155°C. under a constant pressure. The progress of the oxidation can be followed by measuring the decreasing volume of air above the oil.

The deterioration of steam-turbine oils[324] may be measured in a manner similar to that used for transformer oils.[325]

Chebotar[326] has observed that the Sligh and Michie tests measure only the sludge formed by the oxidation of transformer oil and do not take into account the formation of acids. He determined oxidizability by heating the sample in a bomb with oxygen at 151°C. and 300 pounds pressure and noting the pressure drop. The naphthols, naphthylamines and diphenylamines inhibited the oxidation of "Nujol" (a white medicinal oil), but not of transformer oil. On the contrary β-naphthylamine even accelerated the oxidation of the latter oil. Phenyl-α-naphthylamine is not as satisfactory in practice as in the laboratory, according to Typke.[327]

The oxidation of solar oil by air under pressure is catalyzed by the addition of various metal naphthenates. The rate of oxidation is proportional to the pressure and is greater for more highly refined oils.[328]

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[315] N. I. Chernozhukov, M. V. Kurlin and A. M. Kurlina, *J. Appl. Chem. (U.S.S.R.)*, 1936, **9**, 690; *Brit. Chem. Abs.* **B**, 1936, 627; *Chem. Abs.*, 1936, **30**, 7830.

[316] M. V. Kurlin and A. M. Blinova, *J. Appl. Chem. (U.S.S.R.)*, 1934, 7, 831; *Chem. Abs.*, 1935, **29**, 2725; *Brit. Chem. Abs.* **B**, 1935, 134.

[317] J. G. Ford, *Elec. Eng.*, 1936, 55, 371; *Chem. Abs.*, 1936, **30**, 3994.

[318] R. H. Golde, *De Ingenieur*, 1934, **49**, E173; *Chem. Abs.*, 1935, **29**, 5288; *J. Inst. Pet. Tech.*, 1935, **21**, 93A.

[319] H. Weiss and A. Maillard, *Ann. combustibles liquides*, 1935, 10, 437; *J. Inst. Pet. Tech.*, 1935, **21**, 335A.

[320] H. Weiss and T. Salomon, *Ann. combustibles liquides*, 1927, **2**, 801; *Chem. Abs.*, 1928, **22**, 2458.

[321] L. S. Ornstein, C. Janssen, Sr., D. T. J. ter Horst, C. Krijgsman and G. H. Frederik, *Proc. acad. Sci. Amsterdam*, 1936, **39**, 566; *Chem. Abs.*, 1936, **30**, 5775; *Brit. Chem. Abs.* **B**, 1936, 728.

[322] H. Weiss and T. Salomon, *Ann. combustibles liquides*, 1929, **4**, 419; *Chem. Abs.*, 1929, **23**, 5565.

[323] A. Gemant, *Trans. Faraday Soc.*, 1936, **32**, 1628; *J. Inst. Pet. Tech.*, 1936, **22**, 540A; *Chem. Abs.*, 1937, **31**, 842; *Brit. Chem. Abs.* **B**, 1936, 1188.

[324] T. Salomon, *Compt. rend. congr. Graissage (Strasbourg)*, **1932**, 383; *Chim. et ind.*, 1933, **29**, 811; *Chem. Abs.*, 1933, **27**, 3596. Also M. Van Rysselberghe, *15me Congr. chim. ind.* (Bruxelles, Sept., 1935), **1936**, 14; *Chem. Abs.*, 1936, **30**, 5776.

[325] T. Salomon, *Compt. rend. congr. Graissage*, **1931**, 733; *Chem. Abs.*, 1933, **27**, 4661.

[326] L. P. Chebotar, *J. Inst. Pet. Tech.*, 1934, **20**, 168; *Chem. Abs.*, 1934, **28**, 3573; *Brit. Chem. Abs.* **B**, 1934, 309; *J. Inst. Pet Tech.*, 1934, **20**, 255A.

[327] K. Typke, *Erdöl u. Teer*, 1933, **9**, 61; *Chem. Abs.*, 1934, **28**, 5652.

The following have been suggested as antioxidants for transformer oils: polycarboxylic acids or anhydrides such as maleic, succinic or adipic,[329] α-naphthol,[330] naphthylamines and various nitro aromatic compounds,[331] β-naphthol with dibenzyl disulphide,[332] and benzyl disulphide with various substances such as *m*-cresol, thymol monosulphide, 2,2′-dihydroxy-1,1′-dinaphthyl sulphide or 4,4′-dihydroxy diphenyl sulphide.[333]

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[328] K. I. Ivanov and V. I. Shustina, *J. Applied Chem.* (*U.S.S.R.*), 1936, **9**, 82; *Chem. Abs*, 1936, **30**, 6173.

[329] F. M. Clark, Canadian P. 338,340, 1934; *Chem. Abs.*, 1934, **28**, 2178. British P. 423,774, 1935, to British Thomson-Houston Co. Ltd.; *Chem. Abs.*, 1935, **29**, 4574. French P. (addition to 758,072) 44,763, 1935, to Compagnie française pour l'exploitation des procédés Thomson-Houston; *Chem. Abs.*, 1935, **29**, 6416.

[330] J. C. D. Oosterhout, Canadian P. 359,295, 1936, to Texaco Development Corp.; *Chem. Abs.*, 1936, **30**, 6186.

[331] F. M. Clark, U. S. P. 1,988,299, and 1,988,300, Jan. 15, 1935, to General Electric Co.; *Chem. Abs.*, 1935, **29**, 1623; *Brit. Chem. Abs.* **B**, 1935, 1128. Canadian P. 348,447, 1935; *Chem. Abs.*, 1935, **29**, 3508. Canadian P. 353,332, 1935; *Chem. Abs.*, 1935, **29**, 4165. Both to Canadian General Electric Co. Ltd. French P. 758,072, 1934, to Compagnie française pour l'exploitation des procédés Thomson-Houston; *Chem. Abs.*, 1934, **28**, 3152

[332] B W. Story and E. W. Fuller, U. S. P 2,000,105, May 7, 1935, to Socony-Vacuum Oil Co; *Chem. Abs.*, 1935, **29**, 4165; *Brit. Chem. Abs* **B**, 1936, 534.

[333] B. W. Story and E. W. Fuller, U. S. P. 2,028,257, Jan. 21, 1936, to Socony-Vacuum Oil Co; *Chem. Abs*, 1936, **30**, 1989.

Chapter 41

Oxidation of Aromatic Hydrocarbons

Since aromatic hydrocarbons can be isolated from petroleum fractions in some degree of purity by the sulphur dioxide extraction process[1] and by other methods, the oxidation of these compounds is of considerable interest to petroleum chemistry. By careful separation of that fraction of an Oklahoma crude boiling between 107 and 108°C., as much as 32 per cent toluene was recovered.[2]

Various catalysts have been used in the partial oxidation of the aromatics; in general, the oxides of vanadium, tungsten and chromium have been found best suited to the operation. Charlot[3] reported an investigation of the oxides of boron, beryllium, magnesium, aluminum, silicon, titanium, vanadium, chromium, manganese, iron, nickel, cobalt, cadmium, copper, lead, zinc, zirconium, columbium, molybdenum, tin, antimony, tellurium, tantalum, tungsten, thorium, bismuth, thallium, uranium, lanthanum, cerium, praesodymium, neodymium, and samarium. A number of combinations of two or more oxides were investigated, as well as the metallic catalysts such as nickel, copper, lead, cobalt, platinum and palladium. The metals are approximately 50 to 100 times as active for complete oxidation as are the difficultly reducible oxides, but these metals tend to promote destructive total oxidation by this excessive activity. The amount of substance undergoing partial oxidation is independent, over a considerable range, of the time of contact, the concentration, or the nature of the organic substance, according to this investigator. The catalyst employed is the deciding factor.

In the partial oxidation of benzene, Newitt and Burgoyne[4] report, there are only three stages before ring-rupture takes place. They believe that, in the case of benzene, oxidation under high pressure proceeds as a series of hydroxylations, yielding successively phenol, hydroquinone, and finally quinone. With toluene and ethylbenzene under high pressure, the side chain and the ring are oxidized simultaneously. (See page 943.)

A definite induction period occurs in the oxidation of toluene and ethylbenzene although there is none in the oxidation of benzene. On the other hand there is a surface effect[5] in the latter oxidation but none in the case of toluene and ethyl benzene. From these results the investigators concluded that there is a chain mechanism involved in each case, though the mode of propagation differs.

Stephens and Roduta[6] have studied the reactions of more complex alkyl-substituted benzenes, particularly tertiary hydrocarbons, and report that in these cases oxidation always occurs at the α-carbon atom (the side-chain carbon directly ad-

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[1] According to V. A. Kalichevsky and B. A. Stagner "The Chemical Refining of Petroleum," The Chemical Catalog Co., New York, 1933.

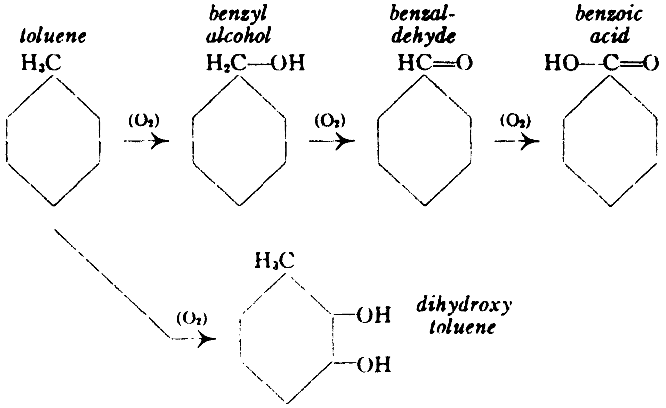
[2] J. H. Bruun, R. T. Leslie and S. T. Schicktanz, *Bur. of Standards J. Research*; 1931, 6, 363; *Brit. Chem. Abs.* B, 1931, 660; *Chem. Abs.*, 1931, 25, 2551.

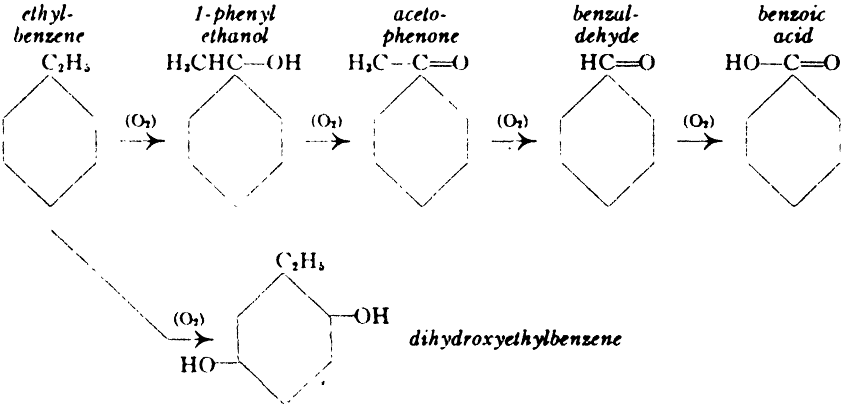
[3] G. Charlot, *Ann. Chim.*, 1934, 2, 415; *Chem. Abs.*, 1935, 29, 1314; *Brit. Chem. Abs.* A, 1935, 43.

[4] D. N. Newitt and J. H. Burgoyne, *Proc. Roy. Soc.*, 1936, A153, 448; *Chem. Abs.*, 1936, 30, 2555; *Brit. Chem. Abs.* A, 1936, 599. See also C. E. Seuseman and J. J. Stubbs, *Ind. Eng. Chem.*, 1933, 25, 1286; *Brit. Chem. Abs.* A, 1934, 62; *Chem. Abs.*, 1934, 28, 746.

[5] In this instance, a greater surface-to-volume ratio retards the reaction. The effect of surface-volume ratios is more fully discussed in Chapter 36.

[6] H. N. Stephens and F. L. Roduta, *J.A.C.S.*, 1935, 57, 2380; *Chem. Abs.*, 1936, 30, 1750; *Brit. Chem. Abs.* A, 1936, 324.





jacent to the ring). With methylethylphenylmethane, methyl-*n*-propylphenylmethane or methyl-*n*-butylphenylmethane, oxidation proceeds to yield acetophenone almost exclusively; if there is any tendency to yield the higher phenones (propriophenone or butyrophenone) the relative yields are so slight the products could not be detected. Experiments with an example of a secondary hydrocarbon, diphenylmethane, showed that oxidation led to benzophenone provided no water was present, but the reaction was inhibited by the presence of water. It was suggested that this was due to reversible decomposition involving the loss of water. On the other hand, in the case of the tertiary hydrocarbons no inhibitory effect was observed either with respect to the previously mentioned tertiary hydrocarbons or to triphenylmethane or methyldiphenylmethane. This may find explanation in the fact that the formation of a molecule of water from a molecule of a primary addition product of oxygen and a tertiary hydrocarbon would require the contribution of one of the hydrogen atoms from an alkyl group. The resulting alkene residue then must drop off if a ketone, which is always the observed product, is formed. The loss of a carbon atom attendant upon the elimination of water may so reduce the probability of reversal of this step by excess of water that no observable inhibition occurs. Evidently, from these results the larger aliphatic group attached to the tertiary carbon tends to contribute the hydrogen and is thus eliminated. In the case of triphenylmethane, where no alkyl groups are available, the oxidation products are benzophenone and phenol.

An investigation of the slow oxidation of benzene in the vapor phase, using ethyl nitrate as a catalyst, has been reported by Griffith and Hill.[7] These investigators found that there was no appreciable induction period in the oxidation, but that the reaction time varied directly with the benzene-oxygen ratio and the pressure, and inversely with the absolute temperature and the concentration of ethyl nitrate catalyst. The surface effect was quite pronounced as the reaction velocity was considerably lowered by increasing the surface-volume ratio. Similarly, the addition of a small amount of tetraethyl lead counteracted the accelerating effect of the ethyl nitrate. In general, it was found that the reaction catalyzed by ethyl nitrate at 430 to 480°C. was similar to the uncatalyzed reaction at 530°C. If concentrations of ethyl nitrate exceeding 0.35 per cent are employed, the reaction becomes explosive, but short of the explosive reaction, the intermediate products are the same as those produced in the purely thermal reaction at a somewhat higher temperature.

However, in the oxidation of benzene and its derivatives and homologues, metallic oxide catalysts are generally employed. Pigulevskii and Yarzhemskaya[8] have studied this reaction and reported that benzene, oxidized in the presence of vanadium pentoxide (on fireclay) at 370 to 450°C., proceeds through benzoquinone to maleic anhydride and then to carbon dioxide and water. For maximum yields of maleic anhydride these investigators recommend high gas velocities through the reaction chamber and rapid cooling of the resultant gases. Under these conditions a yield of about 38 per cent of maleic acid was obtained. Three condensers in series were employed in collecting the reaction products; one air-cooled to room temperature, one cooled to 0°C. in ice water, and a final trap cooled in liquid air. Maleic acid was obtained under these conditions, but when the first (air-cooled) condenser was maintained at 40 to 50°C. to prevent condensation of water vapor, only pure anhydride was collected there. In addition to these principal products, over 4 per cent of quinone was formed and complex decomposition products probably containing quinhydrone. It is suggested that the reaction goes from benzene through hydroquinone, quinone and maleic anhydride to carbon dioxide and water. On the other hand, it has been reported that benzene and benzene derivatives which contain no oxygen (such compounds as toluene and chlorobenzene) can be converted to the corresponding —OH derivatives by heating the former with oxygen or air in the absence of oxidation catalysts but at temperatures between 650 and 750°C.[9]

MALEIC ANHYDRIDE

Downs[10] has pointed out that in the synthesis of organic chemicals, several different inorganic or organic intermediates are usually needed, and frequently the large quantities of the inorganic materials required may exceed the cost of the organic raw material. Catalytic oxidation processes, such as those now used in making maleic anhydride and other benzene oxidation products, approach the ideal for industrial purposes, since only one raw material need be stocked for use; the other is air, which carries no freight or warehousage charges or other costs beyond that of blowing it into the reaction vessel. Maleic acid, before the discovery of its synthesis by oxidation of benzene, was a laboratory chemical and of little practical interest. It is now produced by oxidation of benzene or naphthalene. Maleic acid is one of the reagents indicated in the important Diels-Alder reactions[11] according to which it condenses spontaneously with conjugated diolefins such as butadiene, isoprene, cyclopentadiene and various other unsaturated compounds:

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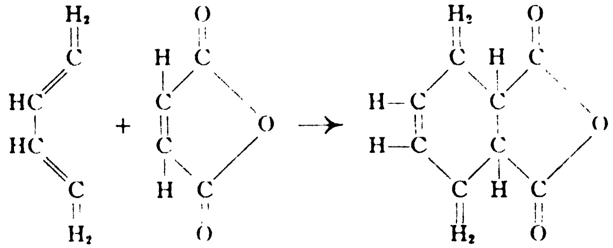
[7] R. H. Griffith and S. G. Hill, *Trans. Faraday Soc.*, 1936, **32**, 829; *Chem. Abs.*, 1936, **30**, 4828; *J. Inst. Pet. Tech.*, 1936, **22**, 299A; *Brit. Chem. Abs.* **A**, 1936, 804

[8] V. V. Pigulevskii and E. J. Yarzhemskaya, *J. Gen. Chem (U.S.S.R.)*, 1935, **5**, 1620; *Brit. Chem. Abs.* **B**, 1936, 536; *Chem. Abs.*, 1936, **30**, 1978.

[9] British P. 439,356, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 2990; *Brit. Chem. Abs.* **B**, 1936, 182. French P. 788,261; *Chem. Abs.*, 1936, **30**, 1390.

[10] C. R. Downs, *Ind. Eng. Chem.*, 1934, **26**, 17; *Chem. Abs.*, 1934, **28**, 1332; *Brit. Chem. Abs.* **B**. 1934, 265.

Butadiene + maleic anhydride ——→ tetrahydrophthalic anhydride



By the direct addition of water to the double bond of maleic acid, malic acid can be produced. This edible acid has been suggested as a substitute for tartaric acid in baking powder. Bertsch and Krause[12] report reducing maleic acid electrolytically to produce succinic acid by hydrogenation of the double bond. The yield is said to be approximately 97 per cent of that theoretically possible.[13]

This oxidation of benzene to maleic anhydride or maleic acid is generally effected by the use of catalysts composed of oxides of metals of variable valence (such as iron, vanadium, chromium and tungsten). Zalkind and Zolotarev[14] mixed benzene and air by bubbling the air through liquid benzene at 15°C., and tested the catalytic action of vanadium pentoxide (deposited on pumice) with this mixture. The gases were preheated to 360°C. and reacted at 410 to 430°C. The investigators reported this process gave the highest yields obtained, approximately 15 per cent of maleic acid calculated on the benzene consumed. Unoxidized benzene was recovered by adsorption on cooled silica gel. It was believed that oxidation proceeded as a series of hydroxylations, yielding phenol, hydroquinone, quinone and finally maleic acid.

Jaeger[15] proposes that the effective yield can be increased without the use of recycling pumps by using a series of reaction chambers interspersed in the circuit between a series of condensers. The reaction product of the first chamber would thus pass through a condenser wherein the oxidation products would be extracted and the unreacted gases would pass on to a second converter, a second condenser, and thus through whatever number of converters was decided upon.

Jaeger[16] has also suggested that maleic acid may be produced by the oxidation of heterocyclic compounds such as furan and its derivatives. Thus, furfuraldehyde and air, mixed with exhaust gases from the oxidation, are passed over a vanadium pentoxide-aluminum oxide catalyst at about 370°C. to yield 45 to 75 per cent of the compounds maleic acid and mesotartaric acid. Polynuclear hydrocarbons such as naphthalene may be used as the starting material in the maleic acid synthesis also. Brode and Johannsen[17] suggest that the vapor of naphthalene or acenaphthene and air be passed over vanadium pentoxide catalyst at 400°C. and the resulting mixture slightly cooled. It is then passed over zinc, cadmium or aluminum oxide catalysts and the products (principally maleic acid and benzene) condensed out of the exhaust gases.

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[11] See Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

[12] J. A. Bertsch and A. H. Krause, U. S. P. 1,945,175, Jan. 30, 1934, to Monsanto Chem. Co.; *Brit. Chem. Abs.* **B**, 1934, 953; *Chem. Abs.*, 1934, **28**, 2370.

[13] It has been reported that succinic or phthalic acid anhydride can be reacted with thionyl chloride in the presence of zinc chloride catalyst to produce the corresponding dicarboxylic acid chlorides. The anhydride is maintained in a liquid state, carrying the zinc chloride catalyst, while the thionyl chloride is added slowly. British P. 414,572, 1934, to Monsanto Chem. Co.; *Chem. Abs.*, 1935, **29**, 478; *Brit. Chem. Abs.* **B**, 1934, 875.

[14] Yu. S. Zalkind and S. Zolotarev, *J. Applied Chem.* (*U.S.S.R.*), 1933, **6**, 681; *Chem. Abs.*, 1934, **28**, 4039; *Brit. Chem. Abs.* **A**, 1933, 1152.

[15] A. O. Jaeger, U. S. P. 1,945,354, Jan. 30, 1934, to Selden Co.; *Chem. Abs.*, 1934, **28**, 2366; *Brit. Chem. Abs.* **B**, 1934, 954.

[16] A. O. Jaeger, U. S. P. 1,995,614, March 26, 1935, to Selden Co.; *Chem. Abs.*, 1935, **29**, 2975; *Brit. Chem. Abs.* **B**, 1936, 444.

PRODUCTION OF PHTHALIC ANHYDRIDE

Phthalic anhydride, important in dye synthesis and other organic syntheses, has become of even greater importance since synthetic resins of the alkyd type have created an excellent market for this substance. The oxidation of naphthalene to produce this substance has, consequently, become of increased importance. As in the oxidation of benzene to its intermediate products of oxidation, the common catalysts in the oxidation of naphthalene to phthalic anhydride are the oxides of the metals capable of more than one valence state. Punnett[18] suggests, for instance, that vanadic oxide and aluminum deposited on alundum be used as the catalytic agent in this type of reaction. The temperature employed is generally somewhat below red heat.[19] Jaeger[20] proposes a similar (vanadium oxide) catalyst supported on diatomite brick. Silicon carbide, titanium carbide or zirconium carbide have been suggested as activators for vanadic oxide catalysts in this reaction[21] and simultaneously serve as supports for the catalyst.[22]

Brode and Johannsen[23] report that one apparatus for the oxidation can be effectively arranged so that the naphthalene vapors and air are led into a catalyst chamber, then to a chamber where the gases are collected, mixed with air, and passed to another catalyst chamber. The exhaust from this second catalyst chamber is mixed with further naphthalene vapor-air mixture, and the gases are passed to a third catalyst chamber (See Fig. 212).

In controlling the proportion of oxygen to naphthalene vapor, Riegler[24] saturates the oxygen-containing gas (air) with naphthalene vapor at a known temperature, then admixes a known quantity of naphthalene-free air to bring the proportions to any desired value. To aid in control determinations of the reaction, Douglass and Jones[25] suggest that a portion of the reacting gases be withdrawn during the process, and the organic constituent be converted completely to oxides of carbon and determined as such. The catalytic converter apparatus is then controlled by these determinations.[26]

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[17] J. Brode and A. Johannsen, U. S. P. 1,963,258, June 19, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5081.

[18] E. B. Punnett, U. S. P. 1,978,506, Oct. 30, 1934, to National Aniline & Chem Co; *Chem. Abs.*, 1935, **29**, 176. See also W. S. Calcott and W. A. Douglass, U. S. P. 2,034,896, March 24, 1936; *Chem. Abs.*, 1936, **30**, 3182.

[19] A. Wohl, U. S. P. 1,971,888, Aug. 28, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 6446.

[20] A. O. Jaeger, U. S. P. 1,935,054, Nov. 14, 1933, to Selden Co.; *Brit. Chem. Abs.* **B**, 1934, 793; *Chem. Abs.*, 1934, **28**, 480.

[21] A. O. Jaeger, U. S. P. 1,930,716, Oct. 17, 1934, to Selden Co; *Chem. Abs.*, 1934, **28**, 172, *Brit. Chem. Abs.* **B**, 1934, 875

[22] R. Klatt and H. Jeliner (*Petroleum Z.*, 1935, **31**, 1; *Chem. Abs.*, 1936, **30**, 2733; *J. Inst. Pet. Tech.*, 1936, **22**, 357A) report that oxidizing a kerosene containing a considerable portion of naphthalene, using a vanadic oxide catalyst, yields almost solely the lowest fatty acids and aldehydes, formic acid, formaldehyde, acetic acid and acetaldehyde and dimethylketone. No phthalic anhydride was reported in this case.

[23] J. Brode and A. Johannsen, U. S. P. 1,959,898, May 22, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 4345.

[24] R. Riegler, U. S. P. 2,030,800, Feb. 11, 1936, to National Aniline & Chem. Co.; *Chem. Abs.*, 1936, **30**, 2208.

[25] W. Douglass and H. L. Jones, U. S. P. 2,013,727, Sept. 10, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 6903.

[26] Phthalic anhydride and phthalic acid derived from it have been suggested as constituents of petroleum-emulsion breaking compounds. C. H. M. Roberts (U. S. P. 1,978,227, Oct. 23, 1934, to Tretolite Co.; *Brit. Chem. Abs.* **B**, 1936, 261; *Chem. Abs.*, 1935, **29**, 329) mixes phthalic acid with

PRODUCTION OF BENZALDEHYDE

Parks and Katz[27] have published a report of data accumulated in studies of a series of different catalytic agents for the oxidation of toluene in air. They were particularly interested in the production of benzaldehyde, since this substance is a lower oxidation product than benzoic acid or maleic anhydride, and correspondingly more difficult to obtain in good yield. The industrial price of benzaldehyde is relatively higher in consequence, and it was hoped that a suitable catalyst could be found which would tend to favor the production of the aldehyde. It was thought that the lead derivatives of the metals of the fifth and sixth groups of the periodic table would favor the partial oxidation of the side chain, since tetraethyl lead slows the oxidation of gasoline. Other investigations had indicated that metals of these groups were best suited for the partial oxidation of toluene. Various catalyst supports were tried, and aluminum metal in granular form was selected as most satisfactory. Because of its high heat conductivity the tendency toward formation of hot spots and consequent irregular oxidation leading to carbon dioxide and water was decreased. Good heat transfer is necessary as well as effective cooling, since the reactions involved are highly exothermic. The following equations illustrate this proportionality among the various possible degrees of oxidation:

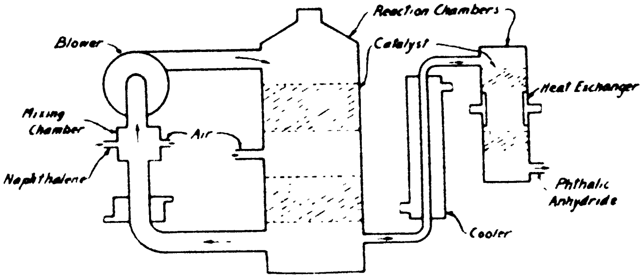

FIG. 212. Sketch of Equipment for Oxidation of Naphthalene to Phthalic Anhydride. (J. Brode and A. Johannsen)

$$C_6H_5CH_3 + \tfrac{1}{2}O_2 \longrightarrow C_6H_5CH_2OH + 39{,}900 \text{ cal.}$$
$$C_6H_5CH_3 + O_2 \longrightarrow C_6H_5CHO + H_2O + 91{,}200 \text{ cal.}$$
$$C_6H_5CH_3 + 3/2\ O_2 \longrightarrow C_6H_5COOH + H_2O + 156{,}300 \text{ cal.}$$
$$C_6H_5CH_3 + 6O_2 \longrightarrow C_4H_2O_3 + 3CO_2 + 3H_2O + 600{,}300 \text{ cal.}$$
$$C_6H_5CH_3 + 9O_2 \longrightarrow 7CO_2 + 4H_2O + 934{,}400 \text{ cal.}$$

In respect to the catalysts it will be remembered that the "gap elements," those possessing more than one oxidation state, have been found most satisfactory, and the hydroxylation theory of oxidation has been most generally accepted in the oxidation of benzene. The hydroxylation mechanism would require the presence of oxygen in the atomic state, and it is found that catalysts removed from the reaction chamber show color shadings indicating various oxidation stages. These investigators conclude that there is an alternate oxidation and reduction of the metallic oxide, atomic oxygen being released in each cycle. The temperature at which a given oxide becomes active in catalyzing the reaction corresponds to the tempera-

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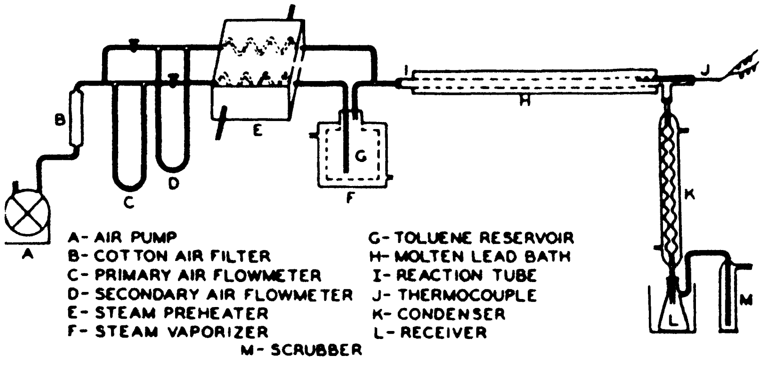
a long chain hydrocarbon sulphonic acid and a sulphur dioxide petroleum extract boiling about 200°C. for this purpose. This investigator has also suggested a reaction product of phthalic anhydride and glycerol partly saponified with ammonia and diluted with alcohol. (U. S. P. 1,977,146, Oct. 16, 1934, to Tretolite Co.; *J. Inst. Pet. Tech.*, 1935, **21**, 25A; *Chem. Abs.*, 1935, **29**, 329.)

[27] W. G. Parks and J. Katz, *Ind. Eng. Chem.*, 1936, **28**, 319; *Chem. Abs.*, 1936, **30**, 2836; *Brit. Chem. Abs.* **B**, 1936, 682; *J. Inst. Pet. Tech.*, 1936, **22**, 202A.

ture at which this oscillation to higher and lower oxides takes place. Among the catalysts tried were lead chromate, tungstate and vanadate, uranium tungstates and molybdates with boron carbide, and other salts and combinations of the metals of the groups suggested. Thus it was found that with lead molybdate a maximum of oxidation was obtained at a temperature of 585°C., when 29.5 per cent of the available oxygen was consumed in partial oxidation products, the remainder of the oxygen producing total oxidation products (carbon dioxide and water). Lead chromate became active as a partial oxidation catalyst at 390°C. (2.4 per cent of the oxygen consumed appeared as oxygenated bodies), although using uranium tungstate, even at 425°C., gave no partial oxidation products. A uranium-molybdenum-boron carbide catalyst at 575°C. gave the highest yield of partial oxidation products, that is, 45 per cent. A similar uranium-molybdenum catalyst without the addition of boron carbide yielded (at 525°C.) only 23 per cent partial oxidation products.[28] The apparatus used is illustrated in Fig. 213.



Courtesy Industrial and Engineering Chemistry

FIG. 213.—Apparatus for Vapor-phase Oxidation of Toluene. (W. G. Parks and J. Katz)

Successful solution-oxidation of toluene to benzaldehyde and benzoic acid has been reported by Berkenheim and his co-workers.[29] The oxidation process in this case is carried out at temperatures of the order of 35 to 40°C. in a sulphuric acid solution, manganese dioxide serving as the source of oxygen. The ratio of benzaldehyde to benzoic acid can be controlled quite accurately, these investigators report, by varying the conditions of time of reaction, temperature, and the ratios of manganese dioxide, sulphuric acid and toluene. Benzaldehyde can be prepared without admixture of benzoic acid by carrying out the reaction at 35 to 40°C. in the presence of 65 per cent sulphuric acid for 6 hours, using 4 parts (by weight) of sulphuric acid and 1 part of manganese dioxide. Toluene is converted to the aldehyde (20 to 22 per cent), and 40 per cent of the toluene can be recovered unchanged. At temperatures of 70 to 75°C., using more sulphuric acid (13 to 14 parts of 50 per cent acid), benzoic acid is the principal product. According to these investigators, manganese dioxide obtained in various ways as by-products can be used satisfactorily in this preparation.

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[28] These yields were calculated on the basis of the oxygen consumed.

[29] A. M. Berkenheim, E. V. Yavorskaya, O. P. Al'bitzkaya and T. F. Dankova, *J. Applied Chem. (U.S.S.R.)*, 1934, 7, 778; *Chem. Abs.*, 1935, 29, 2522; *Brit. Chem. Abs.* B, 1935, 137.

Since benzaldehyde is so readily oxidized to benzoic acid, other investigators[30] have suggested that a milder oxidizing agent be used. Thus, carbon monoxide may be used with benzene, the carbon monoxide adding to the ring to form the aldehyde. The proposed method suggests passing carbon monoxide into an autoclave containing aluminum chloride and benzene which has been saturated with hydrogen chloride at atmospheric pressure. A reaction temperature of 20 to 50°C. is maintained, and the reaction product discharged gradually into water maintained at 10 to 60°C. by circulation of tap water through cooling coils. The investigator reports that the use of ice water, or refrigeration maintaining temperatures near 0°C. is unnecessary.

PRODUCTION OF BENZOIC ACID

Benzoic acid is produced in two types of oxidation processes: by direct oxidation of toluene to the acid, and by oxidation of naphthalene to phthalic anhydride followed by decarboxylation of the dicarboxylic acid to benzoic acid.

The oxidation of toluene to benzoic acid requires powerful methods of cooling, due to the large amounts of heat released during the reaction. Jaeger[31] has suggested a method illustrated in Fig. 214. He has also proposed that an inhibiting vapor, such as carbon tetrachloride, be added as an inert protective.[32] In the oxidation, this investigator found that potassium vanadyl vanadate at 380 to 390°C. acts as a specific catalyst, tending to oxidize the side chain rather than the ring structure. He recommends that milder catalysts, such as a diluted zeolite containing tantalum, molybdenum or tungsten at somewhat higher temperatures (450°C.), be used if aldehydes are desired.[33] It has been reported that the activity of vanadium oxide in this catalytic action can be increased by the addition of silica gel.[34] Jaeger[35] produced a catalyst for this and similar oxidation reactions by mixing together three solutions, one composed of a suspension of "Celite" earth in a water-glass solution, the second a potassium vanadate solution, and the third a solution of potassium aluminate. The mass is converted to a gel by the addition of sulphuric acid and this gel filtered and dried at temperatures below 100°C. It is then broken into lumps, hydrated by trickling water over it, and leached with a 3 per cent sulphuric acid solution. The leached mass is calcined in air mixed with sulphur dioxide gas at 420 to 500°C.

Toluene may be partially oxidized in solutions, particularly solutions of chromates and dichromates, it has been reported. The reaction is carried out under pressure and at temperatures above 100°C. (but below 360°C., the critical temperature of water). The dichromates of the alkali metals should be present, it is said, since in this way the sodium hydroxide formed during the reaction which reduces the chromium is neutralized by the dichromate rather than by the benzoic acid formed. Photochemical reactions also may be employed in this type of partial oxidation. Anthraquinone is generally employed as the catalyst, according to Nozicka,[36] but various auxiliary catalysts may be employed to improve the process.

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[30] J. A. Almquist, British P. 445,554, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 6759.

[31] A. O. Jaeger, U. S. P. 1,942,817, Jan. 9, 1934, to Selden Co.; *Chem. Abs.*, 1934, **28**, 1713; *Brit. Chem. Abs.* **B**, 1934, 816.

[32] A. O. Jaeger, U. S. P. 1,909,355, May 16, 1933, to Selden Co.; *Brit. Chem. Abs.* **B**, 1934, 88. See also U. S. P. 1,909,354, May 16, 1933; *Chem. Abs.*, 1933, **27**, 3725.

[33] A. O. Jaeger, U. S. P. 1,937,962, Dec. 5, 1933, to Selden Co.; *Chem. Abs.*, 1934, **28**, 1056; *Brit. Chem. Abs.* **B**, 1934, 825. See also S. V. Bogdanov and N. S. Leznov, Russian P. 38,633, 1934; *Chem. Abs.*, 1936, **30**, 3445.

[34] J. K. Chowdhury and S. C. Choudhury, *J. Indian Chem. Soc.*, 1934, 11, 185; *Brit. Chem. Abs.* **B**, 1934, 609; *Chem. Abs.*, 1934, **28**, 4297.

[35] A. O. Jaeger, U. S. P. 1,941,688, Jan. 2, 1934, to Selden Co.; *Chem. Abs.*, 1934, **28**, 1713.

[36] F. Nozicka, Austrian P. 141,082, 1935; *Chem. Abs.*, 1935, **29**, 3916. U. S. P. 1,945,067.

He found, for instance, that activated carbon or an oxide or salt of copper, bismuth, iron, vanadium or silver acts as a promoter. The vapors of toluene and anthraquinone mixed with oxygen may be passed over such a catalyst as those suggested, while the gases are strongly irradiated to produce benzoic acid. Similarly, this type of catalyst will promote the reaction of benzene and hydrogen chloride to form chlorobenzene, it is stated.

The second oxidation method of producing benzoic acid mentioned earlier in this chapter is that which involves the oxidation of naphthalene to phthalic anhydride followed by decarboxylation to benzoic acid. Jaeger[37] recommends passing phthalic anhydride, hydrogen and carbon dioxide over sodium chloride on quartz at 360 to 400°C. If phthalic anhydride and carbon monoxide are passed over copper on pumice at this temperature, the product is largely benzaldehyde. With other catalysts such as iron oxide-sodium chloride, aluminum vanadate, hydrated copper aluminum silicate or iron carbonyl, a mixture of benzoic acid and benzaldehyde is produced. This investigator has also suggested passing the oxidation products of naphthalene mixed with water vapor directly over a strongly alkaline contact mass (e.g., copper carbonate-calcium hydroxide on pumice at 320 to 400°C.) for the preparation of benzoic acid.[38] He[39] has further suggested beryllium oxide at 350 to 450°C. as a catalyst in this decarboxylation. According to Brode and Johannsen,[40] the use of lead oxide as catalyst allows the reaction to

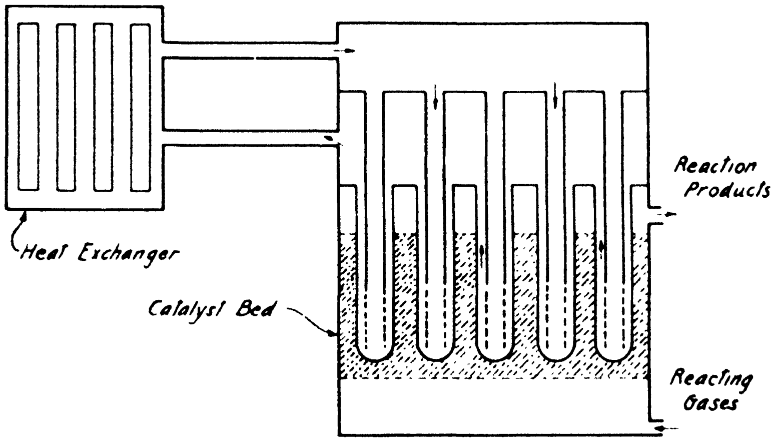

Fig. 214.—Method for Temperature Control in Catalytic Vapor-phase Reactions. (A. O. Jaeger)

Jan. 30, 1934, to Vereinigte Chem. Fabr. Kreidl, Heller and Co.; *Chem. Abs.*, 1934, **28**, 2273. German P. 624,964, 1936, to Vereinigte Chem. Fabr. Kreidl, Heller & Co.; *Chem. Abs.*, 1936, **30**, 4870. See also I. Kreidl, U. S. P. 1,971,042, Aug. 21, 1934; *Chem. Abs.*, 1934, **28**, 6066.

[37] A. O. Jaeger, U. S. P. 1,966,067, July 10, 1934, to Selden Co.; *Brit. Chem. Abs.* **B**, 1935, 443; *Chem. Abs.*, 1934, **28**, 5473.

[38] A. O. Jaeger, U. S. P. 1,964,516, June 26, 1934, to Selden Co.; *Brit. Chem. Abs.* **B**, 1935, 397; *Chem. Abs.*, 1934, **28**, 5080.

[39] A. O. Jaeger, U. S. P. 1,956,718, May 1, 1934, to Selden Co.; *Chem. Abs.*, 1934, **28**, 4071; *Brit. Chem. Abs.* **B**, 1935, 219.

[40] J. Brode and A. Johannsen, U. S. P. 1,982,195, 1,982,196 and 1,982,197, Nov. 27, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 480. U. S. P. 1,955,050, April 17, 1934; *Chem. Abs.*, 1934, **28**, 3744. See also A. O. Jaeger, U. S. P. 1,939,212, Dec. 12, 1933, to Selden Co.; *Chem. Abs.*, 1934, **28**, 1364; *Brit. Chem. Abs.* **B**, 1934, 1825. On the other hand, Brode, Johannsen and Drossback (German P. 608,075, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 2548) have suggested an analogous reaction for production of naphthoquinone and benzene. In this case the

take place at a temperature as low as 250°C., although temperatures up to 500°C. are suggested. The same investigators also proposed bismuth and cadmium oxides, and iron oxide activated by zinc or cadmium oxide. According to Scharff and associates,[41] in the decarboxylation of phthalic anhydride to benzoic acid, cooling considerations are of little importance, since there is small heat exchange in this reaction. Thus, these investigators suggest that the oxidized naphthalene vapors containing phthalic anhydride be passed directly from the reaction chamber (leaving this zone at a temperature of about 400°C.) and, with only slight cooling, contacted with the decarboxylation catalyst. This latter conversion to benzoic acid is, however, attended with the difficulty that organic sulphur compounds present as impurities tend to form sulphuric acid. The inorganic acid is considered to poison the catalysts used in the decarboxylation. They suggest, therefore, that the catalyst be either moved countercurrently to the reacting gases, or that two catalyst stages be employed. In the first proposed method, the raw gases meet first the nearly exhausted, and sulphuric-acid-saturated, catalyst, gradually depositing sulphuric acid as they reach progressively fresher catalyst. In the second method, the gases would first be contacted with a cheap and inferior catalyst such as pumice granules or zeolites, catalysts which will absorb the sulphuric acid.

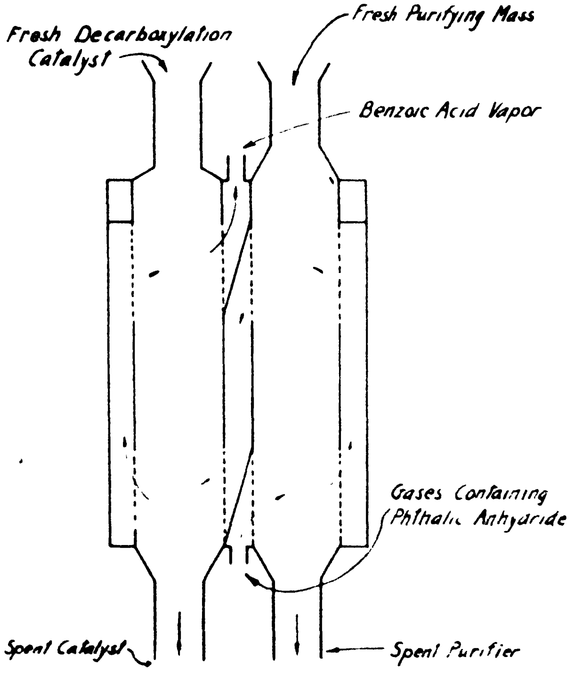

FIG. 215. Sketch of Apparatus for Decarboxylation of Phthalic Anhydride to Benzoic Acid. (M. Scharff, J. Brode, A. Johannsen and J. Reichart)

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products of the catalytic oxidation of naphthalene are led (without isolation) over a decarboxylation catalyst such as cadmium oxide-aluminum oxide at a temperature of 380°C. These investigators have also suggested passing the oxidation products over a second oxidation catalyst with further admixture of air, thus producing maleic acid and benzoquinone.

[41] M. Scharff, J. Brode, A. Johannsen and J. Reichert, U. S. P. 1,988,876, Jan. 22, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1835.

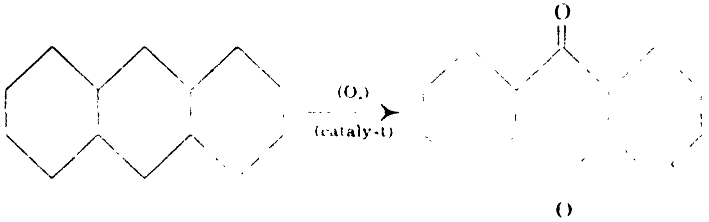
The purified gases are then contacted with a more expensive and highly active catalyst.[42] (See Fig. 215).

Jaeger[43] finds that the metal salts of phthalic acid such as zinc phthalate or nickel phthalate can be similarly broken to yield benzoic acid and some benzaldehyde. Thus zinc phthalate in the presence of quartz is heated with hydrogen to 325-410°C. to yield largely benzaldehyde, but with steam at 360 to 400°C. benzoic acid is the principal product. The efficiency of the reaction is reported to be quite high; with nickel phthalate, hydrogen and steam at 350°C. the yield is 78 per cent of the theoretical quantity of benzoic acid. Daudt[44] reports that phthalic anhydride and water vapor react at temperatures of 175 to 350°C. in the presence of nickel phthalate catalyst to yield benzoic acid.

Jaeger[45] has also suggested that methyl alcohol and phthalic anhydride be passed over a zinc oxide catalyst (at 380 to 400°C.) to produce methyl phthalate and benzoic acid. In a somewhat similar manner dimethyl (or diethyl) phthalate, passed over aluminum vanadate, yields methyl (or ethyl) benzoate and some benzaldehyde.

PRODUCTION OF ANTHRAQUINONE

Various investigators have reported methods for the oxidation of anthracene to anthraquinone. This reaction may be represented as follows:



Anthracene Anthraquinone

Schmidlin[46] found that vanadium oxide or iron or silver vanadate served as catalysts for the air oxidation of fused anthracene under normal pressure. Jaeger[47] also reports that iron vanadate or iron-manganese vanadate makes a good catalyst for this reaction but recommends the addition of an alkali or alkaline earth metal salt, such as one of potassium or calcium. Crude commercial anthracene at a temperature of 340 to 440°C. is mixed with air and passed over this catalyst mass to form anthraquinone. Pietzsch[48] has proposed an apparatus for this type of oxidation wherein the gaseous reactants are passed through annular spaces between an inner tube containing catalyst, and an outer wall surrounded by a heating bath. The flow is then reversed and the gases led countercurrently through the catalyst tube where reaction takes place. DeRewal[49] reports that the vapor phase oxidation of anthracene can be catalyzed by the oxides of nitrogen, using air or other oxygen-containing gas as the source of oxygen.

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[42] C. Conover (U. S. P. 2,006,335, July 2, 1935, to Monsanto Chem. Co.; *Chem. Abs.*, 1935, **29**, 5460) has suggested a different type of decarboxylation, using chromium chloride as the decarboxylation catalyst in the presence of dry hydrogen chloride to produce benzoyl chloride from phthalic anhydride. The metal chloride is added to the acid anhydride at a temperature above 200°C., while the dry hydrogen chloride is passed in.

[43] A. O. Jaeger, U. S. P. 1,961,150, June 5, 1934, to Selden Co.; *Brit. Chem. Abs.* **B**, 1935, **297**; *Chem. Abs.*, 1934, **28**, 4744.

[44] H. W. Daudt, U. S. P. 1,962,175, June 12, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 4744.

[45] A. O. Jaeger, U. S. P. 1,925,590, Sept. 5, 1933, to Selden Co.; *Brit. Chem. Abs.* **B**, 1934, **618**; *Chem. Abs.*, 1933, **27**, 5338.

[46] J. Schmidlin, German P. 578,723, 1933; *Chem. Abs.*, 1934, **28**, 784.

[47] A. O. Jaeger, U. S. P. 1,926,540, Sept. 12, 1933, to Selden Co.; *Brit. Chem. Abs.* **B**, 1934, **711**; *Chem. Abs.*, 1933, **27**, 5751.

[48] K. F. Pietzsch, U. S. P. 1,961,164, June 5, 1934, to Selden Co.; *Chem. Abs.*, 1934, **28**, 4748.

On the other hand, it has been suggested that alkali chromates be made the source of oxygen in producing anthraquinone from anthracene. A solution of the chromates may be made acid by addition of an acid weaker than acetic, such as, for instance, carbonic acid. The anthracene is heated under pressure with this solution, to produce anthraquinone and chromic hydroxide.[50]

ELECTROCHEMICAL OXIDATION OF AROMATIC HYDROCARBONS

In addition to the catalytic methods of oxidation that have been suggested, a number of investigators have found that in some instances electrochemical methods may be employed successfully. McKee and Heard[51] reported an investigation of the oxidation of benzoin in alkaline solutions of sodium aromatic sulphonates. They found that a nickel electrode permitted good efficiency in this oxidation, while in strongly acid solutions naphthalene depolarized a graphite electrode with the formation of quinone and various phenolic products. The solvents used by these investigators were sodium xylene- and cumene-sulphonates. These compounds bring into aqueous solution a considerable variety of water-insoluble organic compounds, including toluene, naphthalene, anthracene, hydroquinone, borneol and non-aromatic compounds such as linseed acids and oleic acid. In addition to making possible the oxidation of these dissolved compounds by electrochemical action, the sulphonates also aided electrochemical halogenation of toluene.

Palfreeman and Knibbs[52] report oxidation of benzene to benzoquinone by adding benzene continuously to a 10 per cent aqueous solution of sulphuric acid in an undivided cell of lead and lead dioxide anode and a water-cooled lead cathode. The acid-benzene mixture was stirred at such a rate as to assure distribution without emulsification. The oxidation product (benzoquinone) in dilute benzene solution overflows from the surface of the acid into a reduction vessel containing iron and an aqueous iron salt kept above the boiling point of benzene. The quinol formed passes into the aqueous phase, while the benzene is distilled, condensed, and returned to the electrolytic cell. Schwaebel[53] suggests that one solution of the problem of getting good contact between the hydrocarbon and the active electrode may be to inject the benzene or other hydrocarbon into the aqueous electrolyte in a finely divided state in such a manner that it rises over the surface of one of the electrodes. For instance, the compound may be forced in through a nozzle arranged beneath an inclined anode of large surface. The benzene then rises across the anode surface to the surface of the aqueous electrolyte, and a pump recirculates the superincumbent liquid through the nozzle. Thus benzene may be oxidized to benzoquinone, or toluene to toluquinone. Analogous electrolytic reduction may be used to convert benzoquinone to hydroquinone.

Plotnikov[54] and co-workers have investigated the oxidation of toluene in ether-water solutions of phosphoric acid and report that the ring and side chain are both attacked. Benzaldehyde can be produced in somewhat better than 1 per cent yields (1.08 per cent) when using current densities of 0.0112 amperes per square centimeter, although low current densities of the order of 0.0065 amperes per square centimeter yield only about 0.1 per cent. Kirk and Bradt[55] report that nitration of toluene can be speeded and made more complete by electrochemical action. Concentrated nitric and sulphuric acids and toluene were placed in the anodic compartment of a cell with a porous diaphragm and a platinum electrode. A nitration yield of 46 per cent without electric current was increased to 48.3 per cent by the application of direct current. However, mixtures which normally give nitration yields higher than 50 per cent do not give better yields with current. The presence of manganous, bismuth, ceric, mercuric, chromic and vanadic ions increase nitration, particularly manganous ions, but tungstic oxide decreases nitration, though all of these serve to increase oxidation. Fichter and Rosenzweig[56] studied the electrochemical reactions of *p*-fluorotoluene and found that although this halogenated toluene is readily oxidized to fluorobenzoic acid, the intermediate aldehyde could not be isolated. Fichter and Müller[57] report that the use of wetting agents such as isopropylnaphthalenesulphonic acid to disperse hydrocarbons (e.g., mesitylene) in dilute aqueous sulphuric acid leads to higher yields of oxidation products. The products of electrolysis (with a current density of 0.016 amperes per square centimeter) on a lead dioxide anode were mesitylenealdehyde, mesitylenic acid, *o*-hydroxymesitylenic acid, uvitic acid, mesitol, 2,6-dimethylbenzoquinone, acetic and formic acids and carbon dioxide. Separate experiments on the individual intermediate products established the course of the reaction. A 13 per cent yield of mesitylenic acid was obtained on the lead dioxide anode, and 6 per cent on a platinum anode in a mixture of 40 per cent nitric acid and 50 cc. of glacial acetic acid plus the wetting agent.

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[49] F. J. DeRewal, U. S. P. 2,022,845, Dec. 3, 1935, to Atmospheric Nitrogen Corp; *Chem. Abs.*, 1936, **30**, 730; *Brit. Chem. Abs.* **B**, 1936, 1195.

[50] British P. 413,366, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 182; *Brit. Chem. Abs.* **B**, 1934, 826.

[51] R. H. McKee and J. R. Heard, *Trans. Electrochem. Soc.*, 1934, **65**, 161; *Brit. Chem. Abs.* **A**, 1934, 496; *Trans. Electrochem. Soc.*, 1934, **65**, 135; *Brit. Chem. Abs.* **A**, 1934, 496; *Chem. Abs.*, 1934, **28**, 2276.

[52] H. Palfreeman and N. V. S. Knibbs, British P. 430,572, 1933; *Brit. Chem. Abs.* **B**, 1935, 796; *Chem. Abs.*, 1935, **29**, 7834.

[53] F. X. Schwaebel, German P. 614,041, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 5754.

[54] V. A. Plotnikov, I. I. Katznel'son and S. G. Fridman, *Mem. Inst. Chem. All Ukrainian Acad. Sci.*, 1934, **1**, 133; *Chem. Abs.*, 1935, **29**, 2094.

Drozdov and Drozdov[58] suggest oxidizing anthracene to anthraquinone electrochemically in a dimethylketone-sulphuric acid solution. They report that in this solution the hydrocarbon combines directly with oxygen at the anode to yield anthraquinone, a reaction which does not occur when using suspensions of anthracene in sulphuric acid. In the latter case, a catalyst such as cerium sulphate or potassium dichromate is needed to transfer the active oxygen, the electrochemical action serving to regenerate the oxidizing agent. Cerium sulphate is a more active transfer agent than potassium dichromate, but the products obtained are contaminated to a greater degree by higher oxidation products of anthracene than is the case when potassium dichromate is used.

Miscellaneous Oxidation Reactions of the Aromatics

Jaeger[59] has reported that fluorene can be oxidized with air in the presence of vanadic oxide catalysts in a manner similar to the oxidation of naphthalene. The reaction takes place between 300 and 500°C. to yield fluorenone and a small amount of phthalic and maleic anhydrides. These latter products can be removed from the oxidation mixture by cooling the exhaust gases to just below 190°C.

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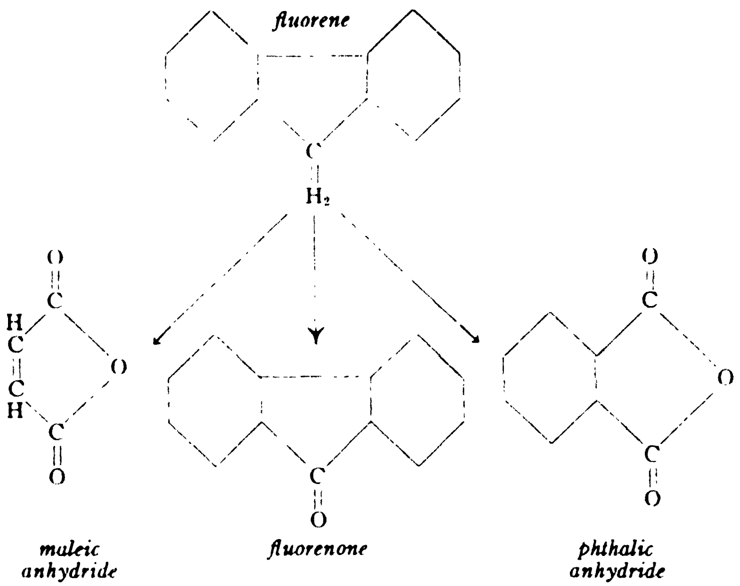
[55] R. C. Kirk and W. E. Bradt, *Trans. Electrochem. Soc.*, 1935, **67**, 285; *Brit. Chem. Abs.* **A**, 1935, 589; *Chem. Abs.*, 1935, **29**, 2860.

[56] F. Fichter and J. Rosenzweig, *Helv. Chim. Acta*, 1933, **16**, 1154; *Chem. Abs.*, 1934, **28**, 2277; *Brit. Chem. Abs.* **A**, 1933, 1152.

[57] F. Fichter and O. Müller, *Helv. Chim. Acta*, 1935, **18**, 831; *Brit. Chem. Abs.* **A**, 1935, 1229; *Chem. Abs.*, 1935, **29**, 6150.

[58] N. S. Drozdov and S. S. Drozdov, *J. Applied Chem. (U.S.S.R.)*, 1933, **6**, 897; *Chem. Abs.*, 1934, **28**, 3985; *Brit. Chem. Abs.* **A**, 1934, 38.

[59] A. O. Jaeger, U. S. P. 1,892,768, Jan. 3, 1933, to Selden Co.; *Brit. Chem. Abs.* **B**, 1934, 55; *Chem. Abs.*, 1933, **27**, 2164.



Duckert[60] reports that acenaphthene can be oxidized to naphthalic acid and acenaphthenequinone to the extent of about 2 per cent by the use of oxygen (as oxidizing agent) and a catalyst. The best conditions were found to be 3 to 5 kilograms per square centimeter pressure, a temperature of 300°C. using as catalyst manganese nitrate, and dissolving the acenaphthene in dichlorobenzene. Kiprianov and Dashevskii[61] found that the oxidation of acenaphthene produced a small quantity of acenaphthenequinone and some naphthalic acid anhydride. A considerable quantity of the quinone could not be separated from the acid anhydride by extraction in aqueous sodium carbonate or sodium acid sulphite solutions, due to the formation of mixed isomorphic crystals of the two organic substances. The isomorphic crystals appeared to consist of alternate layers differing in chemical properties. Extraction and separation was possible by using the sodium salts in aqueous solutions under pressure and at elevated temperature, or by dissolving the salts in hot nitrobenzene. The rather small yields of the quinone were raised by this extraction method.

Dashevskii and Karishin[62] treated acenaphthene (5 gms.) with ammonium dichromate (19 gms.) in 95 per cent acetic acid solution (200 cc.) and obtained a 71.1 per cent yield of acenaphthenequinone, along with only 7.5 per cent of naphthalic acid.

It has been reported that acenaphthene can be dehydrogenated to acenaphthylene by certain catalysts typified by solid, non-reducible heavy-metal compounds such as zinc molybdate and zinc oxide, although magnesium oxide, crystalline silicon or graphite are also suggested. The acenaphthene, with a diluent such as nitrogen or water vapor, is passed over the catalyst at a temperature of 600 to 750°C. under atmospheric pressure.[63]

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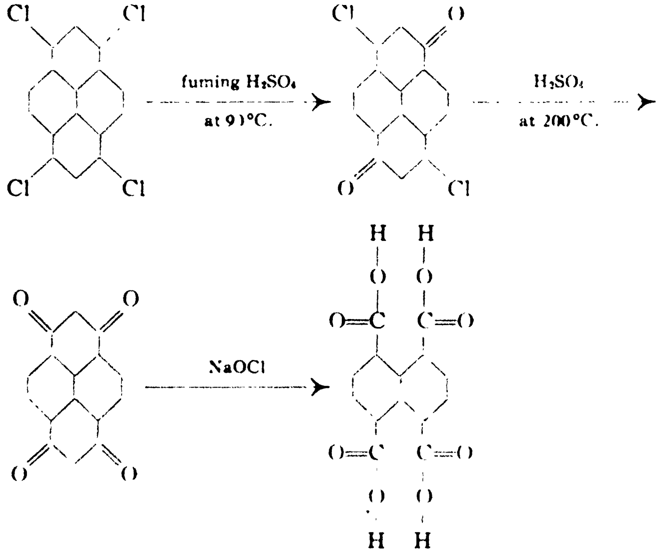
[60] R. Duckert, *Arch. sci. phys. nat.*, 1933, **15**, 244, 343; *Chem. Abs.*, 1934, **28**, 1255; *Brit. Chem. Abs.* **A**, 1933, 1153.

[61] A. I. Kiprianov and M. M. Dashevskii, *J. Applied Chem.* (*U.S.S.R.*), 1934, **7**, 944; *Chem. Abs.*, 1935, **29**, 2530; *Brit. Chem. Abs.* **A**, 1935, 347.

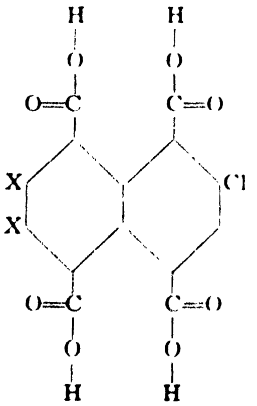
[62] M. Dashevskii and A. Karishin, *Org. Chem. Ind.* (*U.S.S.R.*), 1936, **1**, 729; *Chem. Abs.*, 1937, **31**, 679.

[63] British P. 423,885, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 4382; *Brit. Chem. Abs.* **B**, 1935, 348. French P. 762,672, 1933; *Chem. Abs.*, 1934, **28**, 5081.

More complex aromatic acids may be made by indirect oxidation processes. Thus naphthalene-1,4,5,8-tetracarboxylic acid and its derivatives may be prepared from pyrene. The method proposed involves a preliminary chlorination of pyrene, to form the tetrachloropyrene. This is oxidized in three stages; first in 20 per cent fuming sulphuric acid at 90°C., then in concentrated sulphuric acid at 200°C. The pyrenequinone formed by these processes is then oxidized by sodium hypochlorite, with rupture of two of the rings, to form naphthalene-1,4,5,8-tetracarboxylic acid.



If instead of the tetrachloropyrene, a hexachloropyrene, obtained by a more exhaustive chlorination of pyrene, is used as the starting material, and the third and final oxidation is carried out using nitric acid in place of the hypochlorite solution, a dichlorinated tetracarboxylic acid is obtained. The product appears to consist of a mixture of two acids; the provisional formula assigned to this product is as follows, in which one X represents an atom of chlorine, the other X a hydrogen atom:[64]



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[64] French P. 756,156, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 2018.

Selenium dioxide has been suggested as the oxidizing agent in syntheses involving such hydrocarbons as polynuclear aromatics containing a methyl or methylene group. Thus 2-methylbenzanthrone can be heated under reflux with acetic acid and selenious acid to yield benzanthrone-2-aldehyde.[65] Fisher[66] reported studies of the oxidation of nitrobenzene compounds and benzyl halides refluxed with selenium dioxide. The conditions required for the oxidation of nitrotoluenes are fairly rigorous; 2,4-dinitrotoluene and 2,4,6-trinitrotoluene were unattacked by selenium dioxide in boiling alcohol though oxidation was possible at somewhat higher temperatures. However, *p*-nitrobenzyl bromide was oxidized readily to nitrobenzaldehyde, and benzyl chloride yielded benzaldehyde and a small quantity of benzoic acid. Nitrobenzal bromide (*p*-) was not as readily oxidized as was the benzyl compound but yielded *p*-nitrobenzoic acid. More complex aromatics such as diphenylmethane, 4,4′-dinitrodiphenylmethane and triphenylmethane were not oxidized by selenium dioxide in boiling alcohol, though at higher temperatures the di- and triphenylmethanes were oxidized to benzophenone and triphenylcarbinol, respectively. Firth and Gething[67] found that selenium compounds act as catalysts for oxidation by hydrogen peroxide. Thus, the oxidation of benzaldehyde in the presence of hydrogen peroxide alone is slow under ordinary conditions, but the addition of a small amount of selenium oxychloride materially accelerates the reaction.

Several reactions have been developed whereby carbon monoxide can be directly added to aromatic compounds, which, although not strictly an oxidation process, yields various oxyaromatics. Zerbe and Jage[68] have studied the reactions of various phenol derivatives and homologues with carbon monoxide under pressure and heat. It was found that in the presence of alcohol (methyl or ethyl) sodium phenolate reacts with carbon monoxide to form ethers. Pressures above 30 atmospheres make this reaction quantitative, according to Zerbe and Jage, carbon monoxide absorption beginning at 130°C. and best yields resulting at 180°C. In general, the phenol homologues are more reactive in this synthesis than is phenol itself, the reactivity being changed by the amount and nature of the basic or acidic substituent. It is suggested that carbon monoxide adds to produce a formic ester intermediate. Hey[69] reports that benzene reacts with carbon monoxide in the presence of hydrogen chloride and aluminum chloride-cuprous chloride catalyst to yield benzaldehyde, benzoic acid, and a small quantity of anthracene. Larson[70] suggests that in the aluminum chloride-catalyzed condensation of carbon monoxide and benzene to benzaldehyde, a complex of aluminum chloride and the aldehyde can be used as the catalyst in the initial stages of the reaction. Thus the reaction is begun with fresh benzene and carbon monoxide plus aluminum chloride-aldehyde complex from previous reactions and later completed by the addition of fresh aluminum chloride.

An indirect method permitting the addition of carbon dioxide to naphthalene and its derivatives has been reported. In this case naphthalene is reacted with metallic sodium in the presence of a stable aliphatic monoether (e.g., dimethyl, methylethyl or methylpropyl ether) or mixtures of these with other nonreactive solvents. The product, 1,4-disodiumnaphthalene, is highly reactive and hydrolyzes to form dihydronaphthalene and when treated with carbon dioxide yields the alkali metal salt of dihydronaphthalenedicarboxylic acid.[71]

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[65] F. Kacer, U. S. P. 1,935,949, Nov. 21, 1933, to General Aniline Works; *Chem. Abs.*, 1934, **28**, 776. German P. 557,249, 1932; *Chem. Abs.*, 1933, **27**, 304

[66] C. H. Fisher, *J.A.C.S.*, 1934, **56**, 2056; *Chem. Abs.*, 1935, **29**, 131; *Brit. Chem. Abs.* **A**, 1934, 1353.

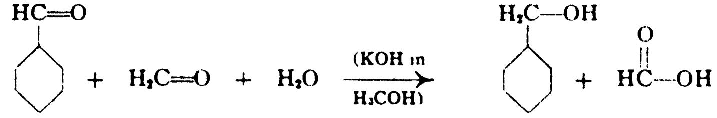
[67] J. B. Firth and H. H. Gething, *J.C.S.*, **1936**, 633; *Chem. Abs.*, 1936, **30**, 5180; *Brit. Chem. Abs.* **A**, 1936, 850.

[68] C. Zerbe and F. Jage, *Brennstoff-Chem.*, 1935, **16**, 88; *Chem. Abs.*, 1935, **29**, 5427; *Brit. Chem. Abs.* **A**, 1935, 442.

[69] D. H. Hey, *J.C.S.*, **1935**, 72; *Chem. Abs.*, 1935, **29**, 1785; *Brit. Chem. Abs.* **A**, 1935, 344.

[70] A. T. Larson, U. S. P. 1,989,700, Feb. 5, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 1834. See also British P. 445,554, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1936, 537.

Davidson and Bogert[72] have reported making benzyl alcohol by the crossed Cannizzaro synthesis. The aromatic aldehyde (e.g., benzaldehyde) is introduced to a solution of methanol and formaldehyde at 65°C. and potassium or sodium hydroxide added, the heat of reaction being absorbed by cooling water to maintain the temperature between 65 and 70°C. The mixture is then heated at 70°C. for 40 minutes and finally refluxed for 20. The aromatic alcohol (benzyl alcohol) is formed in 85 to 90 per cent yield with about 2 to 5 per cent of the corresponding aromatic acid. The reaction is effective also with other aldehydes, permitting the preparation of anisyl, piperonyl and veratryl alcohols.



Separation and Purification of Aromatic Oxidation Products

The problem of separation and purification of the complex mixture of oxidation products resulting from catalytic oxidation processes may be divided into two general phases: separation of the products, and decolorization. The latter is generally effected during the purification, but certain stubborn traces of substances with great coloring power must sometimes be treated separately. The distillable color-bearing substances which come over with phthalic anhydride, for instance, may be removed by prolonged (several hours) heating of the anhydride at about 285°C., but Conover[73] has suggested that this process may be improved by the addition of acids such as lactic, tartaric or citric, or of acid-forming substances such as glycerol. Smith[74] has found the ultraviolet light from a mercury arc aids in decolorization, and it is reported to be sufficiently effective to make further distillations unnecessary in some cases. It has been suggested further[75] that phthalic anhydride vapor be diluted with an inert gas, such as carbon dioxide or nitrogen, so that the anhydride is precipitated in the form of finely divided solid particles, and recovered in this manner.

In the separation of such materials as benzoic acid, phthalic and maleic anhydride and other complex oxidation products, general methods depend on fractional distillation, differential solubility or differential activity. Frequently the distillation is conducted using a compound of the substance to be purified rather than the material itself. Thus, Jaeger and Daniels[76] suggest reacting the crude phthalic anhydride with an ammonium base compound (e.g., ethanolamine) which is capable of reacting with the acid anhydride to form ammonium phthalate. Water is evaporated and the residue heated to form and sublime pure phthalimide. An analogous method involving fractional solidification rather than distillation has been reported. Conover[77] suggests melting the crude product, then cooling it in an undisturbed condition. Crystallization takes place precipitating a purified solid phase while the impurities remain in the liquid, permitting separation. Riegler[78] proposes precooling the vaporous products before condensation. The precooling temperature is adjusted to a controlled value above the dew-point of the mixture with respect to the product. In the products of naphthalene catalytically oxidized for production of phthalic anhydride, the dew-point of phthalic anhydride (though varying considerably since it is dependent on the nature and efficiency of the catalyst, the naphthalene-air ratio originally used, and other factors) is generally in the neighborhood of 115 to 130°C. Thus, a primary cooling apparatus may be used wherein the heat energy of the hot exhaust gases is taken up in boiling water under slightly more than atmospheric pressure. The gases then pass into a condensing chamber where the temperature drops below the dew-point, precipitating the anhydride. The method is said to be advantageous in that it permits the use of a small, closely controlled primary condenser in absorbing the major portion of the heat energy of the exhaust gases. This also permits easy control of the precipitating condenser which is thus required to lower the temperature of the gases to an extent of only a few degrees. The investigator[79] has suggested that the precooled gases (at 120 to 135°C.) be passed through a long, narrow, externally cooled tube, for instance. The tube is fitted with a screw-type scraper, which serves to dislodge the deposit, and simultaneously convey it to the discharge end. At the same time, the flow of gas through the tube is made turbulent by the scraper, resulting in small, homogeneous crystals, it is reported. The gases pass finally through dust bags.

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[71] French P. 779,105, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 4775.

[72] D. Davidson and M. T. Bogert, *J.A.C.S.*, 1935, **57**, 905; *Chem. Abs.*, 1935, **29**, 4344; *Brit. Chem. Abs.* **A**, 1935, 972.

[73] C. Conover, U. S. P. 1,916,657, July 4, 1933, to Monsanto Chem. Co.; *Brit. Chem. Abs.* **B**, 1934, 394; *Chem. Abs.*, 1933, **27**, 4545.

[74] F. D. Smith, U. S. P. 1,948,281, Feb. 20, 1934, to Monsanto Chem. Co.; *Brit. Chem. Abs.* **B**, 1934, 1094; *Chem. Abs.*, 1934, **28**, 2725.

[75] H. B. Foster, U. S. P. 2,064,468, Dec. 15, 1936, to National Aniline & Chemical Co.; *Chem Abs.*, 1937, **31**, 710.

[76] A. O. Jaeger and L. C. Daniels, U. S. P. 1,968,253, July 31, 1934, to Selden Research and Eng. Corp.; *Chem. Abs.*, 1934, **28**, 5835; *Brit. Chem. Abs.* **B**, 1935, 621.

Desai and Patel[80] report an investigation of the solubilities of benzoic, cinnamic, salicylic, phthalic and succinic acids in 14 solvents of various polarities. It was found that in slightly polar solvents, the solubilities decrease with increasing polarity of the solutes, phthalic and succinic acids being scarcely soluble. Solubility increases with polarity in the aromatic hydrocarbons, cyclohexane and carbon tetrachloride. It is suggested that benzoic, cinnamic and salicylic acids form readily dissociable solvates with alcohols, while phthalic and succinic acids form hydrates with water which cause irregularities in the general behavior of these substances. The investigators concluded that the order of solubility is that of the polarity of the solvents in the case of the aromatic hydrocarbons, cyclohexane and carbon tetrachloride, but that this general relationship does not hold with more polar solvents. Chloroform was irregular in all cases. Acetone and butyl alcohol were abnormal in some cases.

This type of differential solubility is used in purifying the various products of aromatic oxidation, either directly applied to the substance or by first forming a separable salt. Jaeger and Daniels[81] have suggested extracting the products with two or more organic solvents and water. The crude compounds are taken up in water solution, the solution is extracted first with a solvent dispersible in water (e.g., hydroxytoluic acid) and this mixture is in turn extracted with a solvent such as benzene which is miscible with the non-aqueous solvent and indispersible in water. The purified acid (maleic, fumaric, phthalic or naphthalic) is recovered from the aqueous solution. Jaeger[82] has also proposed that benzoic and phthalic acids may be separated by washing the mixture with benzene or toluene, in which the benzoic acid is the more soluble. The use of monochloronaphthalene or solvent naphtha in an analogous process has been suggested.[83] On the other hand, Bentley and Catlow[84] have proposed that a double compound be formed by one or more of the constituents of the mixture to be separated and this compound separated out by fractional crystallization. Thus cresols may be reacted with an aromatic amine such as benzidine (paradiaminobiphenyl) and the resulting compound separated from impurities by crystallization. Witzel[85] suggests that in working with the oxidation products of furfural, alkali can be added to form maleic and tartaric salts which can be separated by crystallization from water solution.

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[77] C. Conover, U. S. P. 2,046,368, July 7, 1936, to Monsanto Chemical Co.; *Chem. Abs.*, 1936, **30**, 5597.

[78] R. Riegler, U. S. P. 2,004,586, June 11, 1935, to National Aniline & Chemical Co.; *Brit. Chem. Abs.* **B**, 1936, 633; *Chem. Abs.*, 1935, **29**, 5218.

[79] R. Riegler, British P. 449,621, 1936, to National Aniline & Chemical Co.; *Brit. Chem. Abs.* **B**, 1936, 975; *Chem. Abs.*, 1936, **30**, 8247.

[80] P. G. Desai and A. M. Patel, *J. Indian Chem. Soc.*, 1935, **12**, 131; *Chem. Abs.*, 1935, **29**, 4239; *Brit. Chem. Abs.* **A**, 1935, 695.

[81] A. O. Jaeger and L. C. Daniels, U. S. P. 1,930,054, Oct. 10, 1933, to Selden Co.; *Chem. Abs.*, 1934, **28**, 179; *Brit. Chem. Abs.* **B**, 1934, 751.

Some investigators have suggested accomplishing separation of the impurities by a secondary oxidation process, choosing such conditions as will destroy the undesirable compounds without seriously attacking the desired product. Jaeger and Daniels[86] found this separation applicable where the salts of the desired substance are less readily oxidized by hypohalites than are the corresponding salts of the impurities. The sodium salts (of benzoic, naphthalic or phthalic acids, for instance) are formed, and an aqueous dispersion of these salts is treated with sodium hypochlorite (or hydrogen peroxide). The salts are then converted to esters and separated in the usual manner (as by distillation). Bertsch and Krause[87] report an analogous purification of succinic acid (produced by electrolytic reduction of maleic acid) by the action of alkaline potassium permanganate, followed by decolorization (with charcoal) and filtering. Volkhin[88] reports that phthalic anhydride was purified by maintaining it at 180 to 280°C. for 3 to 4 hours and then adding sodium or calcium chloride with ferric oxide or oxides of other metals (e.g., lead oxide, cuprous oxide). The temperature is maintained at 200 to 280°C. for a further period of 3 to 4 hours and the mixture then distilled in vacuo or blown with air to recover the phthalic anhydride.

On the other hand, Conover[89] suggests separating benzoic and phthalic acids by a partial neutralization with a salt such as sodium carbonate, taking advantage of the fact that phthalic acid is stronger than benzoic. The separation is completed by distilling the resulting mixture with superheated steam.

According to Jaeger[90] most of the impurities present in phthalic anhydride produced by the vapor phase oxidation of naphthalene which are volatile at the sublimation temperature of the acid anhydride are unsaturated substances. He proposes that these substances can be eliminated by contacting them with polymerization catalysts, bringing about the formation of larger and non-volatile molecules. The crude anhydride is heated under atmospheric pressure to its boiling point, or under 3 to 5 atmospheres pressure (when it may be heated to boiling or somewhat less than the boiling point under this pressure). If pressure is used and the vapors are contacted with a polymerization catalyst (aluminum chloride, zinc chloride or activated carbon), the purification process is said to be completed in one to two hours. After the lapse of this period, the refluxing polymerization still is tapped and the phthalic anhydride sublimed over. If atmospheric pressure is used and no catalyst employed, the mass should be maintained at its boiling point (284.5°C.) for 6 hours.

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[82] A. O. Jaeger, U. S. P. 1,919,023, July 18, 1933, to Selden Co.; *Brit. Chem. Abs.* **B**, 1934, 394; *Chem. Abs.*, **1933**, 27, 4817.

[83] British P. 415,748, 1933, to National Aniline & Chemical Co.; *Brit. Chem. Abs.* **B**, 1934, 953.

[84] W. H. Bentley and B. Catlow, U. S. P. 1,980,901, Nov. 13, 1934, to Wm. Blythe & Co., Ltd.; *Chem. Abs.*, 1935, **29**, 476.

[85] H. W. Witzel, U. S. P. 1,945,246, Jan. 30, 1934, to Selden Co.; *Chem. Abs.*, 1934, **28**, 2370; *Brit. Chem. Abs.* **B**, 1934, 953.

[86] A. O. Jaeger and L. C. Daniels, U. S. P. 1,943,892, Jan. 16, 1934, to Selden Co.; *Chem. Abs.*, 1934, **28**, 2019; *Brit. Chem. Abs.* **B**, 1934, 892.

[87] J. A. Bertsch and A. H. Krause, U. S. P. 1,945,175, Jan. 30, 1934, to Monsanto Chem. Co.; *Brit. Chem. Abs.* **B**, 1934, 953; *Chem. Abs.*, 1934, **28**, 2370.

[88] A. E. Volkhin, Russian P. 33,147, 1933; *Chem. Abs.*, 1934, **28**, 3423.

[89] C. Conover, U. S. P. 1,937,383, Nov. 28, 1933, to Monsanto Chem. Co.; *Brit. Chem. Abs.* **B**, 1934, 825; *Chem. Abs.*, 1934, **28**, 1056.

[90] A. O. Jaeger, U. S. P. 1,953,937, April 10, 1934, to Selden Research and Engineering Corp.; *Chem. Abs.*, 1934, **28**, 3744; *Brit. Chem. Abs.* **B**, 1935, 140. See also A. O. Jaeger and K. F. Pietzsch, U. S. P. 1,993,886, March 12, 1935, to American Cyanamid & Chemical Corp.; *Chem. Abs.*, 1935, **29**, 2976; *Brit. Chem. Abs.* **B**, 1936, 47.

Chapter 42

Production of Acids from Petroleum Hydrocarbons

Acids can be obtained by the oxidation of petroleum hydrocarbons by either liquid- or vapor-phase operations. A variety of agents, such as air or oxygen, nitrogen tetroxide, or ozone, have been recommended. In addition to acids, other oxygenated hydrocarbons, such as alcohols, ketones, aldehydes, and esters, are formed and in many instances the conditions under which reaction takes place determine which product will be secured in the largest proportion. In this chapter are discussed those methods applicable to liquid hydrocarbons, particularly to the higher-boiling distillates. Procedures employed with gaseous hydrocarbons have been described previously (see Chapters 37, 38 and 39) and those for solid petroleum hydrocarbons (e.g., paraffin wax) are given later (Chapter 43).

OXIDATION OF LIQUID HYDROCARBONS IN THE LIQUID PHASE

The oxidation of saturated hydrocarbons of petroleum origin, with air and oxygen, has been studied by Burwell.[1] Both liquid and solid materials were oxidized under pressures of 200 to 500 pounds per square inch and at temperatures below the thermal decomposition points of the hydrocarbons, in most cases not above 160°C. Fairly large batches (200 or more pounds) of hydrocarbon materials were oxidized. Those stocks rich in straight-chain hydrocarbons oxidized readily without catalysts, whereas the latter were needed when dealing with mixtures in which other types of hydrocarbons represented the major portion of those present. As catalyst, manganese oleate or a portion of unsaponifiable, partially-oxidized hydrocarbons from a previous treatment was used.

When paraffin wax, melting at 122-124°F. and averaging 24 carbon atoms, was oxidized under the above conditions, most of the acids formed averaged 12 to 14 carbon atoms. On the other hand, by oxidizing distillates from Pennsylvania petroleum, fewer acids and a larger percentage of esters resulted. Monobasic, as well as some dibasic, acids were obtained from the solid paraffins, formic and acetic acids representing 10 to 15 per cent of the total products, with the former predominating. Because of this fact, Burwell concluded that primarily oxidation takes place on the beta-carbon atom, second preference being on the gamma-carbon atom instead of the alpha-carbon.[2] This, he believed, resulted first in the formation of alcohols, and later ketones, which oxidized further, with cleavage, to give acids of lower molecular weight. The reactions are illustrated by the following equations:

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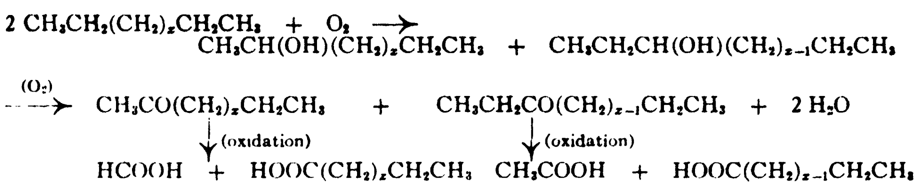
[1] A. W. Burwell, *Ind. Eng. Chem.* 1934, **26**, 204; *Chem. Abs.*, 1934, **28**, 2169; *Brit. Chem. Abs.* **B**, 1934, 438.

[2] At cracking temperatures oxidation attacks the alpha-carbon atom. J. C. Pope, F. J. Dykstra and G. Edgar, *J.A.C.S.*, 1929, **51**, 1875, 2203; *Chem. Abs.*, 1929, **23**, 3436; 3897; *Brit. Chem. Abs.* **A**, 1929, 906, 1036.



$$
\begin{array}{l}
2\,CH_3CH_2(CH_2)_xCH_2CH_3 + O_2 \longrightarrow \\
\qquad CH_3CH(OH)(CH_2)_xCH_2CH_3 + CH_3CH_2CH(OH)(CH_2)_{x-1}CH_2CH_3 \\
\xrightarrow{(O_2)} CH_3CO(CH_2)_xCH_2CH_3 + CH_3CH_2CO(CH_2)_{x-1}CH_2CH_3 + 2\,H_2O \\
\qquad \downarrow \text{(oxidation)} \qquad\qquad\qquad \downarrow \text{(oxidation)} \\
HCOOH + HOOC(CH_2)_xCH_2CH_3 \quad CH_3COOH + HOOC(CH_2)_{x-1}CH_2CH_3
\end{array}
$$

Hydroxy-acids, lactones, alcohols, ketones and esters were also found among the oxidation products. In some cases esters, representing 60 to 75 per cent of the oxidized material, were obtained, which were difficultly saponifiable and were believed to be derived largely from secondary and tertiary alcohols. Although the acids made from the lighter distillates possessed very disagreeable odors, this objectionable feature could be eliminated to a considerable degree by steam distillation. A fraction of these acids boiling as high as 300°C. (572°F.) did not become very viscous even when cooled to —60°F. The corresponding lead, manganese and cobalt salts were readily soluble in gasoline and have found some use as driers.

Various modifications of the above procedure for oxidizing petroleum hydrocarbons have been employed. For example, transformer oil, subjected to a stream of air (for 6 months) at 110-115°C. gave a humic acid-like product which contained numerous hydroxyl and methoxyl groups, and on further oxidation with potassium permanganate yielded benzene-carboxylic acids.[3] On the other hand, if the oxidation of petroleum oils is carried out in several stages of 12 to 24 hours duration each, using calcium naphthenate as catalyst, water-white acids are obtained.[4] According to Plisov and co-workers[5] calcium naphthenate catalyzes the oxidation of gas oil at mild temperatures (115 to 120°C.) to produce hydroxy acids. In a method described by these workers, a yield as high as 90 per cent was reported. The hydrocarbon was mixed with 0.2 per cent calcium naphthenate, and conducted with air through an electrically heated glass tube. The reaction product was agitated with 20 per cent sodium hydroxide, and the mixture centrifuged for 5 minutes to bring about separation. The alkaline solution was extracted with petroleum ether to remove unsaponifiable material, and the raffinate decomposed to yield the free acids. These investigators report that good separation may be obtained by selective solvent action of petroleum ether, taking advantage of the fact that the hydroxy acids are insoluble in this hydrocarbon solvent. In another procedure, after the oxidation is partially completed the conditions are made less intense, for instance, by lowering the temperature, so that secondary reactions involving the first-formed organic acids are retarded.[6] Also by stopping the reaction while some unoxidized material still remains, the formation of polybasic acids is avoided.[7]

The oxidation of a petroleum oil may be made to yield not only the higher oxidation products such as aldehydes and acids, but also lower oxidation products suitable for use as automobile fuels, Penniman[8] states. This investigator proposes an oxidation process which involves passing air through a deep layer (more than three feet in depth) of oil at a temperature between 315 and 482°C. Pressure greater than atmospheric is recommended. Under these conditions, the air is completely deoxygenated before reaching the surface of the liquid. The converted products of the reaction separate into two layers. The lower aqueous layer consists of a water solution of alcohols, acids, aldehydes and ketones. The upper layer is reported to yield a motor fuel of high antiknock value. This oxidation is said also to remove sulphur compounds as sulphur dioxide. Likhushin, Nasumyan and Levkopulo,[9] working with a specimen of Surakhany fuel oil, found that the most favorable temperature for its air-oxidation was 130°C. while the best air rate was 0.3 cubic meters per hour per kilogram of feed stock. Several catalysts were employed, the best of which was sodium naphthenate. This was needed only for initiation of the reaction. They found also that refined oils gave better results by oxidation than did untreated oils. Both, however, exhibit induction periods which are much longer for the latter types of oils.[10]

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[3] N. A. Orlov and I. Z. Ivanov. *J. Applied Chem.* (*U.S.S.R.*), 1935, **8**, 903; *Brit. Chem. Abs.* **B**, 1935, 1032; *Chem. Abs.*, 1936, **30**, 4506.

[4] Z. Danilovich and T. Dianina, *Masloboino-Zhirovoe Delo*, **1935**, 15; *Brit. Chem. Abs.* **B**, 1936, 403; *Chem. Abs.*, 1935, **29**, 5255.

[5] A. K. Plisov, V. P. Golendeev and A. I. Zel'tzburg, *J. Applied Chem.* (*U.S.S.R.*), 1936, **9**, 841; *Chem. Abs.*, 1936, **30**, 7827; *Brit. Chem. Abs.* **B**, 1936, 728.

[6] C. Beck and H. Diekmann, U. S. P. 1,932,613, Oct. 31, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 490.

[7] C. Beck and H. Weissbach, German P. 581,829, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1054.

[8] W. B. D. Penniman, U. S. P. 1,995,324, March 26, 1935; *Brit. Chem. Abs.* **B**, 1936, 438; *Chem. Abs.*, 1935, **29**, 2972.

Keunecke and Werner[11] report that liquid-phase oxidation of hydrocarbons (containing 10 or more carbon atoms) may be inhibited to some extent by the presence of polymerizable impurities. These investigators suggest that if the liquid material to be oxidized is pretreated with approximately 3 per cent of an anhydrous hydrolyzable halide (e.g., aluminum chloride, boron trichloride or silicon tetrachloride), the undesirable substances are precipitated as polymerization products. In some cases it is advantageous to subject the liquids to a desulphurizing treatment prior to oxidation.[12] This is effectively accomplished by hydrogenation under pressures of 5 to 200 atmospheres and at temperatures of 200 to 350°C. Sulphur is removed as hydrogen sulphide and the unsaturated compounds are partially or completely converted into the corresponding saturates. In still other instances, hydrogenation may be substituted by a sulphonation treatment.[13] After extraction of the sulphonic acids, the oil is then subjected to oxidation at 96-115°C. in the presence of a manganese or calcium catalyst. Other contact agents which have been employed in liquid-phase operations include lithium oleate and aluminum stearate, sodium and aluminum palmitates[14] and alkaline-earth carbonates or mixtures of alkaline-earth oxides and alkali carbonates.[15] Also compounds containing several condensed nuclei, or derivatives of these, have served as catalysts in the photochemical air-oxidation of hydrocarbons,[16] as for example, dihydrodianthrone in the transformation of petroleum to fatty acids. Activated carbon, lead, mercury and zinc compounds have been used as oxidation catalysts.[17] Plisov and Goldovskii[18] state that solar oils can be oxidized by air without the aid of a catalyst. The crude oil was atomized together with steam, into a reactor at 210 to 220°C. The distillate obtained consisted chiefly of higher fatty acids, in good yields. The total yield may be increased when water vapor is absent, but the quality of the product

[9] K. P. Likhushin, V. Nasumyan and N. Levkopulo, *Azer. Neft. Khoz.*, 1934, No. 10, 77; *Chem. Abs.*, 1935, **29**, 6034; *Brit. Chem. Abs.* **B**, 1936, 631.

[10] K. I. Ivanov and V. I. Schustina, *J. Applied Chem.* (*U.S.S.R.*), 1936, **9**, 82; *Brit. Chem. Abs.* **B**, 1936, 435; *Chem. Abs.*, 1936, **30**, 6173.

[11] E. Keunecke and R. Werner, German P. 624,229, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 2577.

[12] W. Dietrich and M. Harder, U. S. P. 2,003,584, June 4, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 4772.

[13] G. S. Petrov, *Trans. VI Mendeleev Congr. Theoret. Appl. Chem.*, 1932, **2** (1), 844; *Chem. Abs.*, 1936, **30**, 3975.

[14] W. Dietrich and M. Luther, U. S. P. 2,000.222, May 7, 1935; *Chem. Abs.*, 1935, **29**, 4164. German P. 621,979, 1935; *Chem. Abs.*, 1936, **30**, 2361. Both to I. G. Farbenind. A.-G.

[15] G. S. Petrov, Russian P. 31,928, 1933; *Chem. Abs.*, 1934, **28**, 3575.

[16] I. Kreidl, C. Rosen and K. Rutter, British P. 403,954, 1933; *Brit. Chem. Abs.* **B**, 1934, 232; *Chem. Abs.*, 1934, **28**, 3306. French P. 739,711, 1932; *Chem. Abs.*, 1933, **27**, 2098. F. Nozicka, U. S. P. 1,945,067, Jan. 30, 1934; *Chem. Abs.*, 1934, **28**, 2273. All to Verein. Chem. Fabr. Kreidl, Heller & Co.

[17] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934.

[18] A. K. Plisov and B. Goldovskii, *J. Applied Chem.* (*U.S.S.R.*), 1936, **9**, 492; *Chem. Abs.*, 1936, **30**, 7543; *Brit. Chem. Abs.* **B**, 1936, 627.

under these conditions is poorer. A second oxidation of the unreacted oil also results in improved yields.

OXIDATION OF LIQUID HYDROCARBONS IN THE VAPOR PHASE

Klatt[19] has reported experiments on the vapor-phase oxidation of a kerosene oil. The oxidation was carried out in an electrically heated steel tube packed with various catalysts, the resulting vapors then passing into a condenser arranged for very rapid cooling of the gases. It was believed that rapid cooling would minimize secondary reactions. Manganese dioxide, vanadium pentoxide, iron and brass turnings and aluminum scraps were tested for catalytic activity. The data led him to believe that vanadium is most suitable for the reaction. Manganese dioxide leads to pyrolysis rather than to oxidation, it was found. The investigator concluded that the optimum conditions required the presence of steam, vanadium oxide catalyst, and comparatively mild temperatures (250 to 500°C.). The addition of steam to the air-hydrocarbon mixture served to hasten condensation of the water-soluble compounds produced, and to minimize secondary reactions. Klatt and Jelinek[20] oxidized a specimen of Russian kerosene, containing a large proportion of naphthenes, in the vapor phase with air at 440°C. Steam was added and the mixture passed over a vanadium pentoxide-pumice catalyst. The product consisted of a solid fraction of high-molecular weight fatty acids, a water-soluble portion containing the lower fatty acids, aldehydes and ketones, and a liquid cut of unchanged kerosene. The total yield of fatty acids amounted to 7.5 per cent.

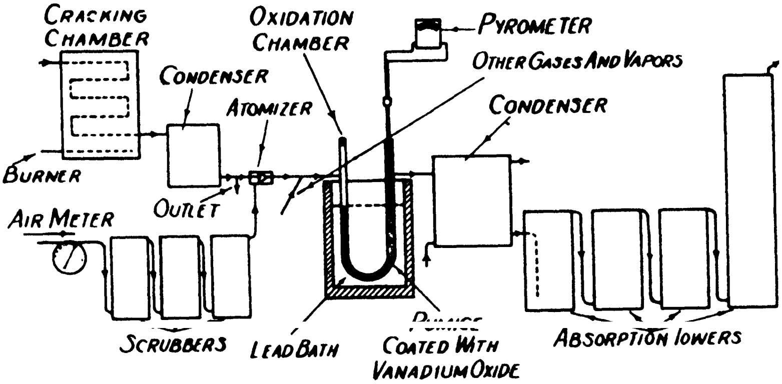

FIG. 216.—Flow Scheme for Partial Oxidation of Cracked Petroleum Distillates. (Carleton Ellis)

Another procedure consists of spraying a mist of cracked petroleum oil, with air, into a reaction zone filled with vanadium oxide catalyst, the temperature being kept below a red heat.[21] As an example, kerosene was introduced into cracking coils heated to 500-600°C. and the vapors then led into air-cooled condensers. The higher-boiling fractions were condensed and the lighter constituents then mixed with air and cooled to room temperature, before entering the reaction chamber, in order to prevent the reaction from becoming too violent. In this way the formation of carbon was retarded. Furthermore, as a result of the cooling prior to oxidation, the products of cracking were partially condensed to a mist. The fine droplets thus formed were not so readily oxidized as material completely in the vapor phase, so that the tendency for excessive oxidation to occur was reduced. The reaction tube, containing vanadium oxide-impregnated pumice, was maintained at 425-450°C. Organic acids, aldehydes and the like were formed. Among the products, phthalic anhydride was identified. Some of these could be converted directly, by use of phenol or resorcinol, into phthalein dyes.

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[19] R. Klatt, *Petroleum*, 1934, **30**, No. 12, 1; *Brit. Chem. Abs.* **B**, 1934, 438; *Chem. Abs.*, 1934, **28**, 4883; *Petroleum*, 1934, **30**, No. 13, 1; *J. Inst. Pet. Tech.*, 1934, **20**, 305A; *Brit. Chem. Abs.* **B**, 1934, 438.

[20] R. Klatt and H. Jelinek, *Petroleum*, 1935, **31**, No. 42, 1; *Brit. Chem. Abs.* **B**, 1936, 83; *Chem. Abs.*, 1936, **30**, 2733.

[21] Carleton Ellis, U. S. P. 1,992,691, Feb. 26, 1935, to Ellis-Foster Co.; *Chem. Abs.*, 1935, **29**, 2730; *Brit. Chem. Abs.* **B**, 1936, 136.

Weber[22] prepared intermediates from petroleum which could be used advantageously in oxidation processes. He subjected a specimen of kerosene to cracking at various temperatures and later oxidized the products with air. The oxidation was accomplished with the aid of a vanadium oxide catalyst mass which was heated in a lead bath at 750°F. James[23] reports that the heat of reaction engendered in the vapor-phase oxidation of petroleum hydrocarbons can be controlled if a series of reaction catalyst-zones is employed, each zone bringing about a fraction of the total oxidation to be carried out. Blue oxides of molybdenum or uranium oxides are suggested as catalysts, and the reaction is to be carried out at a temperature just below red heat. The reaction may be further controlled by the addition of a diluent such as steam or exhaust gases to the mixture of petroleum vapor and air. Mitscherling[24] proposes a photochemical oxidation process for the conversion of hydrocarbons in the vapor or liquid phase. The hydrocarbon material in the vapor phase, for instance, is contacted with a solid catalyst (such as activated charcoal, copper sulphate, carbonate or hydroxide deposited on pumice, or sodium acid sulphite) in the presence of the radiation from a positive-column neon lamp. Cracking processes similar in nature are reported as well. The radiating lamp may contain argon, krypton or other noble gas. The lamp may consume from 180 to 300 watts of electric energy at 12,000 to 15,000 volts.

Nitrogen oxides may also be used as catalysts in the air oxidation of petroleum fractions. Sheely and King[25] treated the vapors of a cleaner's naphtha at 400°C. with air and nitric acid vapors. The acid vapor catalyst was regulated as to its concentration by the temperature of the liquid acid, the pressures of the vapors present ranging from 21 to 68 mm. The products consisted of aldehydes and acids of 8 to 10 carbon atoms. Up to 20 per cent yields of aldehydes were obtainable, while acid yields as high as 90 per cent were reported.

REFINING OF OXIDATION PRODUCTS OF HYDROCARBONS

When petroleum hydrocarbons are oxidized with air, several types of oxygenated derivatives are formed, including carboxylic and hydroxy-carboxylic acids, lactones, estolides[26] (intermolecular esters of hydroxy-carboxylic acids), alcohols, ketones and other oxidized bodies, along with unoxidized hydrocarbons. These products may be separated and refined in several ways. For instance, the crude oxidation products may be subjected to distillation whereby the lower-boiling constituents are separated from those of higher boiling points. The high-molecular-weight acids thus obtained may then be further refined by hydrogenation.[27] In order to effect a separation of saponifiable and unsaponifiable matter, the oxidation product is agitated with lime and then distilled, under conditions such that the calcium salts are not decomposed while the volatile unsaponifiable matter is removed.[28] In the vapor-phase oxidation of petroleum hydrocarbons, certain low-molecular weight acids are formed which remain in the non-condensed gases issuing from the coolers. These gases are sent through scrubbers filled with calcium hydroxide and the volatile acids removed as their calcium salts.[29]

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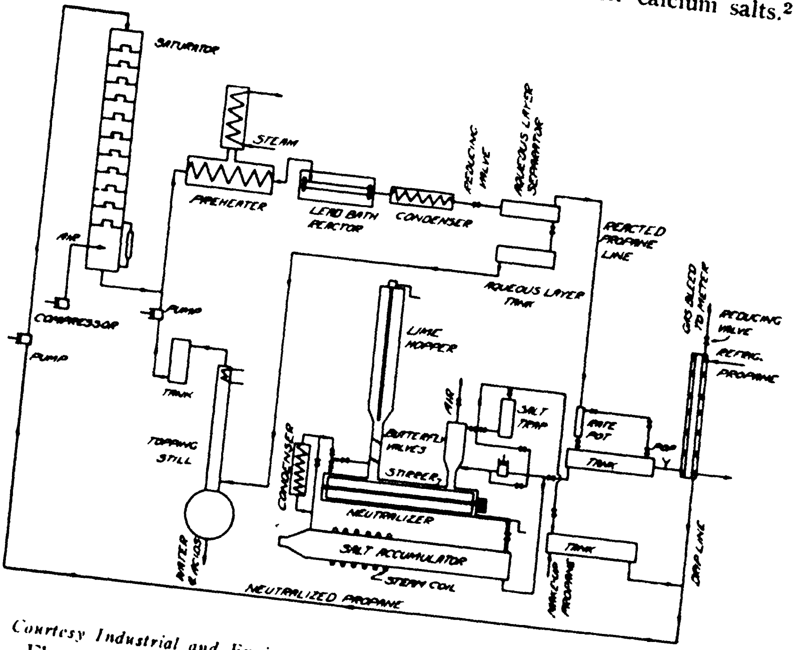
[22] H. M. Weber, U. S. P. 1,516,756, Nov. 25, 1924, to Ellis-Foster Co.; *Chem. Abs.*, 1925, 19, 397.

[23] J. H. James. U. S. P. 2,036,215, April 7, 1936, to C. P. Byrnes; *Chem. Abs.*, 1936, 30, 3627.

[24] W. O. Mitscherling, U. S. P. 2,003,303, June 4, 1935, to Neon Research of Connecticut, Inc.; *Chem. Abs.*, 1935, 29, 4771. U. S. P. 2,003,898, June 4, 1935; *Chem. Abs.*, 1935, 29, 4931.

[25] C. Q. Sheely and W. H. King, *Ind. Eng. Chem.*, 1934, 26, 1150; *Chem. Abs.*, 1935, 29, 1061; *Brit. Chem. Abs.* A, 1934, 1335.

[26] For the structure of estolides and other methods of refining oxidized petroleum, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.



Courtesy Industrial and Engineering Chemistry

FIG. 217.—Flow Diagram for Production of Acids by Direct Oxidation of Propane. (P. J. Wiezevich and P. K. Frolich) (See Chapter 37.)

Another method for removing oxidized from unoxidized bodies, as well as a separation of oxygenated bodies of various oxygen contents, involves the use of liquid sulphur dioxide.[30] At low temperatures (—45°C.) this liquid dissolves principally the acids present. At somewhat higher temperatures the alcohols and aldehydes are dissolved. At even higher temperatures, but still below the normal boiling point of liquid sulphur dioxide (—8°C.), the latter extracts olefins and aromatic substances. By a careful control of the temperature and the proportion of sulphur dioxide, a fractional extraction can be accomplished.

It has been found that if liquids such as water, benzine, benzene or trichloroethylene are sprayed, in a finely divided form, into the crude acids heated to temperatures between 150° and 300°C., and under pressures of 10 to 50 mm., an almost quantitative separation of fatty acids from hydroxy-carboxylic acids is effected.[31] In this manner, the fatty acids are obtained in the distillate and the hydroxy acids in the still residue. Besides being applicable to mixtures of acids, the above process may also be used in refining crude oxidation products which have received no previous treatment.

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[27] M. Harder, German P. 591,121, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 2369.

[28] W. P. Bitler, U. S. P. 1,948,161, Feb. 20, 1934, to C. P. Byrnes; *Chem. Abs.*, 1934, **28**, 2723; *Brit. Chem. Abs.* **B**, 1934, 1094.

[29] J. H. James, U. S. P. 1,912,484, June 6, 1933, to C. P. Byrnes; *Brit. Chem. Abs.* **B**, 1934, 185; *Chem. Abs.*, 1933, 27, 4239.

[30] J. H. James, U. S. P. 1,970,535, Aug. 14, 1934, to C. P. Byrnes; *Brit. Chem. Abs.* **B**, 1935, 664; *Chem. Abs.*, 1934, **28**, 6156.

In case it is preferred to convert the hydroxy into unsaturated acids, the crude acids are heated to 150-250°C. for several hours in the presence of agents which promote dehydration, such as mineral acids, sulphonic acids or zinc chloride.[32] The heating may be carried on in an atmosphere of hydrogen or carbon dioxide. By this treatment the solubility of the acids in petroleum ether, and their iodine numbers, are increased. At the same time the tendency for pitch-formation during subsequent distillation is greatly diminished. As an example, 500 parts of the product obtained by oxidizing gas oil at 150°C. with air, are treated for 4 hours at 250°C. under a pressure of 50 atmospheres with hydrogen and finely-divided nickel, in the presence of 5 parts of naphthalene monosulphonic acid. Lighter-colored acidic bodies (480 parts) are obtained. The two materials show the following differences:

	Solubility in Petroleum Ether	Iodine Number	Pitch Obtained on Distillation
Initial material. . . .	58.2%	17.8	20%
Treated material.	91.8%	46.7	3%

The crude acids, obtained from oxidized petroleum by any of the above methods, may be further separated into high- and low-molecular weight acids by treating their alkali salts with calcium hypochlorite. The calcium salts of the low-molecular weight acids are removed by washing with water, the salts of the high-molecular weight acids remaining undissolved.[33]

USES OF OXIDATION PRODUCTS OF PETROLEUM

Top oils, which reduce the breaking-in time of internal combustion engines and diminish carbon accumulation, are made from certain of the oxidation products of petroleum. These top oils are added to the fuels used in such engines and tend not only to furnish extra lubrication for the valves and pistons but also to soften carbon deposits. As an example, 3 per cent of an oxidized fraction of Pennsylvania petroleum oil is added to 97 per cent of unoxidized paraffin oil, and 1 volume of the mixture is added to 200 volumes of the fuel. The oxidized oil employed for this purpose contains esters, alcohols and ketones, and is neutral in character. Compositions containing these neutral oxidation products are also blended with crankcase lubricants.[34]

Lubricating oils may be incorporated in the soaps formed from the oxidation products of aliphatic petroleum hydrocarbons. The solid or semi-solid compositions thus prepared are proposed as lubricating greases. Or, the free acids, of average molecular weight of 160 to 165, may be dissolved in petroleum distillates to give oils possessing marked penetrating qualities.[35]

[31] H. Franzen and G. Kunze, U. S. P. 1,977,988, Oct. 23, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 179.

[32] W. Dietrich, U. S. P. 1,940,400, Dec. 19, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, :354.

[33] G. S. Petrov and A. I. Danilovich, Russian P. 33,627, 1933; *Chem. Abs.*, 1934, **28**, 3575.

[34] A. W. Burwell, U. S. Patents 1,690,768 and 1,690,769, Nov. 6, 1928; *Chem. Abs.*, 1929, **23**, 509; *Brit. Chem. Abs.* **B**, 1929, 199. U. S. P. 1,863,004, June 14, 1932; *Chem. Abs.*, 1932, **26**, 4169. All patents to Alox Chemical Corp. See also, A. W. Burwell, "Oiliness," Alox Chemical Corp., Niagara Falls, N. Y.

[35] A. W. Burwell, U. S. P. 2,012,252, Aug. 20, 1935; *Chem. Abs.*, 1935, **29**, 6752; *Brit. Chem. Abs.*

The alkali salts of monocarboxylic acids have also been suggested for use in the preparation of certain liquid dispersions such as insecticidal and fungicidal plant-sprays, presumably of the insecticide-in-water type. On the other hand, the free acids have been employed in breaking emulsions of the water-in-oil type.[36] The products formed by chlorinating these acids have also been used for the latter purpose.[37]

The water-insoluble, petroleum-soluble saturated monocarboxylic acids (containing up to 12 carbon atoms) prepared from petroleum are said to act as activating materials in rubber vulcanization.[38] Acids obtained from paraffin oil can be condensed with phenol and formaldehyde or furfural to produce plastic compounds.[39] The polycarboxylic acids which are formed from petroleum can be condensed with polyhydric alcohols to produce resinous bodies also.[40]

B, 1936, 800. U. S. P. 1,895,374, Jan. 24, 1933; *Brit. Chem. Abs.* **B**, 1934, 9; *Chem. Abs.*, 1933, **27**, 2572. Both patents to Alox Chemical Corp.

[36] A. W. Burwell, U. S. P. 1,955,052, April 17, 1934; to Alox Chemical Corp.; *Chem. Abs.*, 1934, **28**, 3830; *Brit. Chem. Abs.* **B**, 1935, 200. U. S. P. 1,993,646, March 5, 1935; *Chem. Abs.*, 1935, **29**, 2730.

[37] C. H. M. Roberts, U. S. P. 1,979,347, Nov. 6, 1934, to Tretolite Co.; *Brit. Chem. Abs.* **B**, 1935, 891; *Chem. Abs.*, 1935, **29**, 329.

[38] A. W. Burwell, U. S. P. 1,981,822, Nov. 20, 1934, to Alox Chemical Corp.; *Chem. Abs.*, 1935, **29**, 644; *Brit. Chem. Abs.* **B**, 1935, 1006.

[39] G. S. Petrov and N. B. Kruglaya, *Plastichcskie Massui*, 1935, No. 3, 16; *Chems. Abs.*, 1936, **30**, 1147.

[40] French P. 764,948, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 6003.

Chapter 43

Oxidation of Paraffin Wax

As the multitude of publications bear witness, much work has been done on the oxidation of paraffin wax and related substances with air and oxygen, as well as with other oxidizing agents. These reactions can be controlled so as to furnish predominantly either alcohols or acids or other oxygen-containing bodies. In spite of the fact that these various types of oxygenated compounds have been made, there still exists some doubt as to the exact structures of the hydrocarbons comprising paraffin wax.

The acidic materials resulting from the oxidation of high molecular weight paraffins have been utilized principally for the manufacture of soaps. Other products, such as esters, have been employed as beeswax substitutes and in miscellaneous preparations (Chapter 45). Although fat-like bodies have been obtained by the oxidation of paraffins[1] and by esterification of the higher aliphatic alcohols with acids of petroleum origin,[2] nevertheless it is questionable from an economic viewpoint whether the manufacture of synthetic fats from petroleum could compete with natural fats, except possibly in times of extreme emergency.[3] For instance, during the World War, German soldiers were fed 6000 tons of synthetic fats made by esterifying ethyl alcohol with the acids formed by the ozonolysis and subsequent heating of unsaturated hydrocarbons resulting from the low-temperature distillation of coal.[4]

Because of the complexity of the oxidation products of paraffin wax and the uncertainty of the nature of its components, the term "wax acids" seems best suited for the acids produced therefrom.

OXIDATION WITH AIR

For the production of wax acids, oxidation of paraffin wax with air appears to be the most economical.[5] Temperatures employed generally ranged from 150° to 180°C., though higher temperatures can be used. Under the latter conditions more vigorous oxidation occurs, accompanied by larger yields of lower molecular weight, or more volatile, products. The application of increased pressures often aids in speeding up the reaction. The velocity of reaction is affected also by the grade of feedstock being treated. For example, Reiner[6] reported that paraffin wax (m.p. 52.5°C.) was more rapidly converted (by air) to acids than ceresin wax (m.p. 56°C.), and that in both instances the change was faster at 140°C. than at 120°C. It has been proposed to refine the hydrocarbons with sulphuric acid and a small proportion of oxides of nitrogen prior to oxidation.[7] Refining conditions, however, should be sufficiently mild to avoid the occurrence of objectionable reactions with the hydrocarbons.

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[1] W. Pungs, German P. 488,877, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, **24**, 2323.

[2] H. H. Franck, *Chimie et industrie*, 1934, **31** (Spec. No.), 889; *Brit. Chem. Abs.* **B**, 1934, 634; *Chem. Abs.*, 1934, **28**, 6005.

[3] R. Furness, *J.S.C.I.*, 1921, **40**, 63R; 1923, **42**, 358; *Chem. Abs.*, 1923, 17, 2966.

[4] A. W. Burwell, *Ind. Eng. Chem.*, 1934, **26**, 204; *Chem. Abs.*, 1934, **28**, 2169; *Brit. Chem. Abs.* **B**, 1934, 438.

[5] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. See also, M. Friedwald, *Rev. pet.*, 1935, No. 612, 4; *J. Inst. Pet. Tech.*, 1935, **21**, 132A; *Chem. Abs.*, 1935, **29**, 3502.

[6] St. Reiner, *Erdöl u. Teer*, 1933, **9**, 412; *Chem. Abs.*, 1933, **27**, 5954; *J. Inst. Pet. Tech.*, 1933, **19**, 469A.

Orlov and Tishchenko[8] noted the formation of volatile acids, aldehydic bodies and a considerable proportion of an asphaltic mass during treatment of paraffin wax (m.p. 57°C.) at 120-140°C. with air. On further oxidation with air (by weathering) the asphalt yielded substances which closely resembled natural humic acids. The development of dark-colored, resinous materials may be avoided by continuously withdrawing the partially oxidized wax and adding fresh wax to the reaction zone.[9] At a lower temperature (52°C.), other investigators obtained both fatty and hydroxy acids as well as their anhydrides, lactones, and lactides.[10] Hydroxy acids corresponding in composition to $C_{13\text{-}17}H_{26\text{-}34}(OH)COOH$ and one whose formula was believed to be $C_{35}H_{69}(OH)COOH$ were identified. The latter acid, whose lactone melted at 58-59.4°C., was prepared by hydrolysis of its methyl ester (m.p. 46-48°C.).

Varlamov[11] found that the employment of catalysts, manganese, nickel, chromium, and cobalt, resulted in higher yields of acids but the proportion of hydroxy acids was also increased. The alkali carbonates were found to be negative catalysts.

Friedolsheim and Luther suggest treatment of paraffin wax at 120° to 180°C. with air in the presence of alkalies such as sodium hydroxide or carbonate.[12] A small proportion of manganese naphthenate or zinc stearate may be added. Under these conditions 70 per cent of the wax is said to be converted into acids. Other metallic catalysts which have been used in the liquid-phase oxidation of paraffin wax include calcium, barium, and magnesium naphthenates,[13] and heavy-metal cinnamates,[14] carbonyls, carbides or palmitates,[15] and stearates.[16]

Burwell[17] investigated the oxidation of saturated petroleum hydrocarbons, with air and oxygen, under various pressures and at temperatures below the cracking temperatures of the hydrocarbons. The air-oxidations were carried out under about 15 to 40 atmospheres pressure and at 120° to 180°C., usually, however, below 160°C. Manganese oleate or unsaponifiable, partially oxidized hydrocarbons were used as catalysts. Paraffin wax melting at 122° to 124°F. and averaging twenty-four carbon atoms gave acids corresponding to an average of twelve to fourteen carbon atoms. By using large quantities of initial hydrocarbons (200 pounds), it was possible to isolate and identify many of the low-boiling volatile acids formed. Among those identified were formic, acetic, propionic, butyric and valeric and others up to 10-carbon acids. In the wash waters were found lactic, and succinic and other dibasic acids. Alcohols, ketones, lactones and esters were also formed. The proportion of the latter, in some cases, was believed to represent a large part of the oxidation products. By use of charges of not less than 1000 pounds of wax many products of commercial utility were obtained.[18]

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[7] M. Harder and W. Dietrich, German P. 619,113, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 484.

[8] N. A. Orlov and V. V. Tishchenko, *J. Appl. Chem.* (*U.S.S.R.*), 1933, **6**, 112; *Chem. Abs.*, 1933, **27**, 5748; *Brit. Chem. Abs.* B, 1933, 613.

[9] E. Peukert, U. S. P. 1,987,208, Jan. 8, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1430.

[10] P. P. Schoruigin and A. P. Kreschkov, *J. Gen. Chem.* (*U.S.S.R.*), 1933, **3**, 825; *Brit. Chem. Abs.* A, 1934, 510; *Chem. Abs.*, 1934, **28**, 6106.

[11] V. Varlamov, *Masloboino-Zhirovoe Delo*, **1932**, No. 6, 47; *Chem. Abs.*, 1933, **27**, 5955; *Brit. Chem. Abs.* B, 1934, 262.

[12] A. v. Friedolsheim and M. Luther, U. S. P. 1,981,384, Nov. 20, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 592.

[13] G. S. Petrov, A. I. Danilovich, and A. Yu. Rabinovich, German P. 584,110, 1933; *Chem. Abs.*, 1934, **28**, 308.

[14] M. Luther and H. Beller, U. S. P. 1,965,962, July 10, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5656.

[15] W. Dietrich and M. Luther, U. S. P. 2,008,490, July 16, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 5855.

[16] M. Luther and W. Flemming, German P. 612,952, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 6244.

[17] A. W. Burwell, *Ind. Eng. Chem.*, 1934, **26**, 204; *Chem. Abs.*, 1934, **28**, 2169; *Brit. Chem. Abs.* **B**, 1934, 438.

From this work it was noted that those materials containing a high percentage of straight-chain hydrocarbons oxidized readily but that other specimens, low in these compounds, required catalysts. From the products formed it was concluded that the principal reaction involved the beta-carbon atom rather than the primary and that the second preference was for the gamma-carbon atom, and so on toward the center of the molecule. It is interesting to note, however, that at higher temperatures (cracking temperatures) the alpha-carbon atom is more susceptible to oxidation than is the beta, the initial products being aldehydes.[19]

Yukhnovskii and Rokhlin,[20] studying the oxidation of petrolatum, found calcium naphthenate to be a better catalyst than magnesium naphthenate. By carrying out their oxidations under 3 to 4 atmospheres pressure they could reduce the reaction time by as much as 500 per cent and considerably lessen the air consumption. The optimum reaction temperature was 110-115°C. At higher temperatures more gasoline-insoluble material was formed. At higher pressures the proportion of hydroxy acids was increased without an increase in the total yield of acids. On the other hand, 160°C. has been reported as the optimum temperature for the air-oxidation of paraffin wax under atmospheric pressure.[21] However, Davanakov and Fedotova[22] report that the catalytic action of the ordinary metallic soaps is effective only at the lower temperatures (i.e., 120 to 140°C. but not at 160°C.). The catalysts used by these investigators were prepared by the interaction of salts of the metals used (manganese, calcium, aluminum) with the fatty acids of paraffin oxidation at 160°C. The calcium catalysts were more effective than the aluminum, and the manganese still more active. In semi-commercial experiments, it was found that the manganese catalysts increased the rate of reaction at 120°C. by a factor of ten. At 140°C., the reaction in the presence of this catalyst left only 15 per cent of unsaponifiable matter. Davanakov[23] reports, further, that the influence of catalysts is increased not only by lower temperatures, but also by the use of less highly refined paraffin.

Berlin and Kuznetzova[24] subjected samples of foots oil, containing various proportions of paraffin wax, to oxidation with air at 160-170°C., both in the presence and absence of naphthenate catalysts. When dealing with oils of high wax content (above 85 per cent) they found that the oxidation proceeded smoothly without catalysts, whereas, oils of lower wax content needed catalysts in order to produce satisfactory yields of oxidation products. It has been suggested that the oil content of petrolatum or slop wax be reduced by extraction with low-boiling hydrocarbons, e.g., propane or butane, admixed with non-solvents for wax, such as alcohols, ketones or chlorinated hydrocarbons.[25] After distillation, the wax may be subjected, in the liquid phase, to oxidation with air. In an attempt to elucidate the function of catalysts in these air oxidations of paraffin waxes, Plisov[26] studied the formation of peroxides and acids during the reaction, both when catalysts (sodium and calcium salts of naphthenic and higher fatty acids) were present, and in their absence. It was found that when catalysts were not present, the amount of peroxides formed increased slowly at first, then rapidly, to a maximum value reached in about 3 hours, and then decreased. After 5 to 6 hours, no peroxides could be detected. In the presence of catalysts, the concentration of peroxides did not pass through a maximum, but declined steadily to zero after 4 to 5 hours.

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[18] A. W. Burwell, U. S. P. 1,690,768 and 1,690,769, Nov. 6, 1928; *Chem. Abs.*, 1929, **23**, 509. U. S. P. 1,791.711, Feb. 10, 1931; *Chem. Abs.*, 1931, **25**, 2019; all to Alox Chemical Corp.

[19] J. C. Pope, F. J. Dykstra and G. Edgar, *J.A.C.S.*, 1929, **51**, 1875, 2203; 1931, **53**, 3752; *Brit. Chem. Abs.* **A**, 1929, 906, 1036; *Chem. Abs.*, 1929, **23**, 3436, 3897.

[20] G. Yukhnovskii and S. Rokhlin, *Masloboino-Zhirovoe Delo*, **1934**, No. 9-10, 8; *Chimie et industrie*, 1935, **34**, 402; *Chem. Abs.*, 1935, **29**, 7629; *Brit. Chem. Abs.* **B**, 1936, 1191.

[21] H. Pflugk, *Braunkohlenarch.*, 1932, No. 37, 1; *Chem. Zentr.*, 1932, **2**, 3959; *Chem. Abs.*, 1933, **27**, 2423.

[22] A. B. Davanakov and O. Y. Fedotova, *Org. Chem. Ind.* (*U.S.S.R.*), 1936, **1**, 79; *Chem. Abs.*, 1936, **30**, 5400.

[23] A. B. Davanakov, *Trans. VI Mendeleev Congr. Theoret. Applied Chem. 1932*, 1935, **2** (1), 867; *Chem. Abs.*, 1936, **30**, 3975.

[24] R. I. Berlin and A. N. Kuznetzova, *Groz. Neft.*, 1935, **5** (1), 52; *J. Inst. Pet. Tech.*, 1936, **22**, 108A, *Chem. Abs.*, 1936, **30**, 3975.

[25] British P. 434,311, 1934, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1935, 1034.

In some cases it is desirable to restrain the extent of oxidation and thus to obtain considerable amounts of aldehydes and alcohols rather than acids. This has been accomplished by oxidizing paraffin wax in the presence of orthoboric and acetic acids.[27] Under these conditions the products are found to contain relatively large proportions of alcohols as their boric acid esters, in which form they are apparently protected against further oxidation. The esters are separated from unreacted paraffin by extraction with ethyl alcohol. After evaporation of the solvent, the residue of wax-alcohol borates is repeatedly extracted with boiling water until hydrolysis is complete and all boric acid removed. A mixture of crude alcohols, prepared in this manner from hard paraffin wax, had the following characteristics:

Crude Wax Alcohols

Melting point	34°C.
Acid number	11
Ester number	27
Saponification number	38
Acetyl number	198
Ash	0.01%

By saponifying, extracting the soap solution with ether, and evaporation of the latter, the crude alcohols were freed of fatty acids. The refined alcohols then exhibited the following properties:

Refined Wax Alcohols

Specific gravity (50°C.)	0.860
Melting point	31.5°C.
Acid number	0.9
Ester number	6.5
Saponification number	7.4
Hydroxyl number	165

Arsenious or phosphorous acid may be used as the oxidation catalyst in place of boric acid.

Several means have been employed for lowering the air-consumption of these oxidation operations, as for instance, by effecting reaction under increased pressures.[28] Another procedure consists of lengthening the period of contact between the air and hydrocarbon.

Friedolsheim and Luther[29] passed molten paraffin wax and air concurrently through a multiple-section heated tower (See Fig. 218.) Among advantages of this method of oxidizing wax is that the partially oxidized hydrocarbons are carried along in contact with air of decreasing oxygen content, thereby diminishing the tendency for excessive oxidation reaction to occur. Diluent gases may also be used to serve the latter purpose. In other instances the reactants are conducted through filler bodies[30] in order that they may become more intimately mixed. Various other methods, such as spraying the liquid hydrocarbons into the top of the reaction vessel and air through the bottom, and the use of high-speed stirrers, have been suggested.[31]

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[26] A. K. Plisov, *Bull. soc. chim.*, 1936, 3 (5), 425; *Brit. Chem. Abs.* A, 1936, 586; *Chem. Abs.*, 1936, 30, 3975.

[27] T. Hellthaler and E. Peter, U. S. P. 1,947,989, Feb. 20, 1934; German P. 552,886, 1934; German P. 564,196, 1934, all to A. Riebeck'sche Montanwerke. A.-G.; *Chem. Abs.*, 1934, 28, 2722, 5832.

[28] G. Yukhnovskii and S. Rokhlin, *loc. cit.*

[29] A. v. Friedolsheim and M. Luther, U. S. P. 1,990,229, Feb. 5, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1832.

USE OF OTHER OXIDIZING AGENTS

In place of air, the oxides of nitrogen (particularly nitrogen dioxide), nitric acid, potassium permanganate, and ozone have been used for the oxidation of paraffin wax.[32] Electrochemical methods may be employed also, though reaction appears to be much slower and in some instances the products are contaminated with a substantial proportion of unsaponifiable material and resins which are difficult to eliminate.

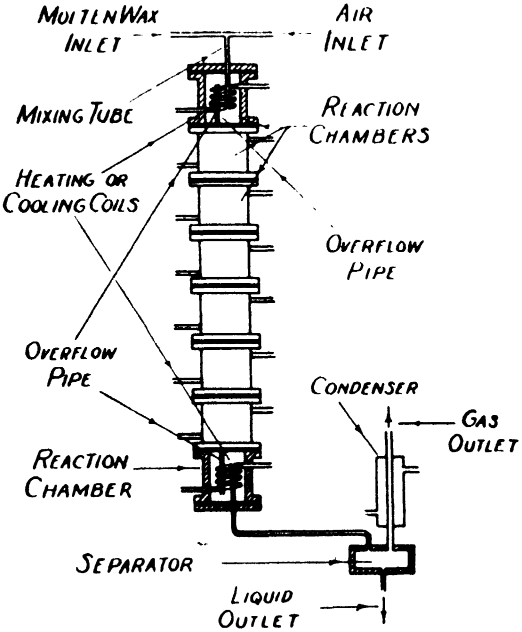

FIG. 218. Tower of Chambers for Paraffin Wax Oxidation. (A. v. Friedolsheim and M. Luther)

Beck and Diekmann[33] point out that higher yields of acids are obtainable if reaction of paraffin wax and aqueous nitric acid is carried out under pressure, or if nitrogen dioxide is passed into the reaction mixture. It was their belief that nitrogen dioxide, not nitric acid, was the principal oxidizing agent and that by maintaining a high concentration of this dioxide oxidation was accelerated. As an example, paraffin wax melting at 52°C. was oxidized in a chrome-nickel-steel tower at 80°C. and under 4 atmospheres pressure with 50 per cent nitric acid. The acid, in a finely divided state, was allowed to trickle through the molten wax while nitrogen dioxide (NO_2) was blown in at the bottom of the tower. By releasing the pressure, nitric oxide (NO) escaped from the top. The final oxidation product, which possessed an acid number of 210 and a saponification number of 290, contained 3 per cent by weight of nitrogen and 15 per cent by weight of unoxidized hydrocarbon. By saponification the nitrogen compounds and unreacted paraffin were removed. The wax acids were then further purified by distillation.

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[30] M. Luther and K. Goetze, U. S. P. 2,015,347, Sept. 24, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 7685.

[31] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[32] For a review of the methods employing these agents, see Carleton Ellis, *loc. cit.*

[33] C. Beck and H. Diekmann, German P. 579,988, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1046.

Carboxylic acids, particularly those having an acid value greater than 400 and prepared by the oxidation of paraffin wax with nitric acid or oxides of nitrogen, may be esterified with monohydroxy alcohols or phenols to furnish softening and gelatinizing agents.[34] Partial esterification of polyhydroxy alcohols, or their ethers, gives the same type of products. These may be incorporated in lacquers, films and plastics (e.g., nitrocellulose or various synthetic resins) to impart plasticizing or softening action.

MISCELLANEOUS OXIDATION REACTIONS

Sapropels[35] can be oxidized with nitric acid to give 30-60 per cent yields of oxidation products which consist of carboxylic acids and their saponifiable derivatives. The acids are of high molecular weights, low in hydrogen and iodine numbers and soluble in petroleum ether. The last-named property apparently indicates only a small proportion of hydroxy acids.

Zherdeva and associates[36] investigated the oxidation of ceresins (m.p. 85-90°C.) from Grozny, Surakhany and Turkmenia. The specimens were blown with air at 160-170°C. for 6 hours. Gasoline-soluble acids were obtained in 30-48 per cent yields, along with 3.7-12 per cent of hydroxy acids. The gasoline-soluble portions had acid numbers of 107-151, saponification numbers of 137-192, and melting points of 41-72.5°C.

SEPARATION OF OXIDIZED FROM UNOXIDIZED MATERIALS

This separation can be accomplished by several means. For example, the oxidation products may be heated, under pressure, with alkalies to above 200°C. in the presence of hydrogen.[37] The hydrogen may be evolved from suitable substances added to the alkali. It is also advantageous to add hydrogenation catalysts to the mixture since some water is likely to be split off the hydroxy acids giving unsaturated acids. The unsaponifiable matter is then removed by extraction with methyl alcohol, isopropyl alcohol, or benzine.[38] Instead of alkali hydroxides, in some cases, the alkaline earth hydroxides, as aqueous suspensions, may be used.[39] In order to convert even the lactones, esters, estolides and lactides to their alkali metal salts, oxidized paraffin is heated, in an autoclave, with 20 per cent alkali carbonate, at temperatures ranging from 60°C. to 300°C. and under pressures of 1 to

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[34] British P. 395,340, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1933, 906; *Chem. Abs.*, 1934, **28**, 483. French P. 739,528, 1932; *Chem. Abs.*, 1933, **27**, 2299.

[35] D. A. Shvedov, S. A. Kuzin and A. I. Andreeva, *Khim. Tverdogo Topliva*, 1934, **5**, 107; *Chem. Abs.*, 1934, **28**, 5961. *Masloboino-Zhirovoe Delo*, 1934, No. 5, 30; *Chem. Abs.*, 1936, **30**, 1739. D. A. Shvedov, Russian P. 4,161, 1924; *Chem. Abs.*, 1928, **22**, 4790. The sapropels are naturally occurring oily or wax-like decomposition products of marine plants and animals, and contain some paraffin material. (L. Litinsky, *Petroleum-Z.*, 1921, 17, 437; *Chem. Abs.*, 1921, **15**, 3739.)

[36] L. Zherdeva, E. Kogan and G. Shiryaeva, *Azer. Neft. Khoz.*, 1934, No. 9, 70; *Chem. Abs.*, 1935, **29**, 6036.

[37] British P. 433,780, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 637; *Brit. Chem. Abs.* B, 1935, 939.

[38] H. Franzen, H. Beller and M. Luther, U. S. P. 1,943,427, Jan. 16, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 2017.

[39] M. Luther and H. Franzen, German P. 576,160, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 490.

15 atmospheres.[40] Or, the procedure may be reversed, whereby the oxidized wax is dissolved in an inert organic solvent, such as diethyl ether or benzine, and the resulting solution then extracted with an aqueous solution of an alkali or organic base which dissolves the saponifiable material.[41] The aqueous layer is separated and extracted with fresh portions of organic solvent. The soaps are then recovered by the evaporation of their aqueous solutions or the wax acids are liberated by acidification of the soap solutions by means of mineral acids. One method consists of introducing dilute nitric acid into the bottom of a tank containing a soap solution so that the organic acids formed may float to the surface where they are protected from further contact with the incoming acid.[42] Carrier and Reeves[43] report a separation of the saponifiable from the unsaponifiable constituents of a mixture resulting from the oxidation of wax, using ammonia and solvent extraction. Saponification with ammonia is carried out under pressure (80 pounds per square inch) at 140 to 150°C. in the presence of water and alcohol (e.g., isopropanol), for two hours. The resultant mixture is then extracted with gasoline, to remove the unsaponifiable matter. The aqueous alcohol solution contains the saponified matter, and this solution is steam distilled to drive off ammonia, water and the alcohol. The residue is treated with sulphuric acid to free the fatty acids and hydrolyze any acid amides which have been formed, and the fatty acids separated from the resulting aqueous solution. An analogous process has been suggested by Beller and Schellmann,[44] who employ an alkali or alkaline earth metal in the saponification step, in the form of an oxide, hydroxide or carbonate.

In order to produce wax acids free from hydroxy acids, oxidized wax is heated, under pressure and above 200°C., in the presence of alkaline substances such as sodium or calcium hydroxide and in an atmosphere of hydrogen. Water is split off during the reaction giving the salts of unsaturated acids.[45] Harder[46] suggests that a similar result may be attained by treating the mixed products of oxidation of a wax with an alkali such as sodium hydroxide and water, together with an agent which will release hydrogen in alkaline media (e.g., zinc dust) at a temperature above 260°C. Ittner[47] suggests employing reduced pressures and temperatures above 250°C. Simultaneously, the mixture is blown with steam, carbon dioxide, or the vapors of toluol or xylol. Oxidation products of petroleum which possess disagreeable odors and which give soaps of poor lathering properties, are, by the above treatment, converted into almost odorless acids which furnish soaps of desirable sudsing properties. Soaps made from the acids thus obtained are also more easily salted out than are the original hydroxy-acid soaps and when blended with higher-grade laundry soaps, may be used in larger proportions without producing soaps which are undesirably soft. Another procedure for dehydrating hydroxy acids consists of heating the calcium soaps in benzene, at 250° to 292°C., using an autoclave. In this manner the hydroxy-acid salts lose water to give the corresponding unsaturated compounds.[48] If the acids thus produced are of objectionable color, they may be dissolved in naphtha and treated with concentrated sulphuric acid, followed by active clay. This results in acids of improved color.[49]

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[40] H. Beller and M. Luther, U. S. P. 1,931,859, Oct. 24, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 490.

[41] British P. 433,305, 1934 (f.), to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1935, 939.

[42] C. Beck and H. Diekmann, German P. 578,779, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 922.

[43] E. W. Carrier and E. D. Reeves, U. S. P. 2,052,165, Aug. 25, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 6938.

[44] H. Beller and M. Schellmann, U. S. P. 2,055,095, Sept. 22, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*. 1936, **30**, 7586.

[45] H. Beller and M. Schellmann, U. S. P. 2,059,201, Nov. 3, 1936; *Chem. Abs.*, 1937, **31**, 419; British P. 433,780, 1935; *Brit. Chem. Abs.* **B**, 1935, 939. Both patents to I. G. Farbenind. A.-G.

[46] M. Harder, U. S. P. 2,059,232, Nov. 3, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, **31**, 419.

[47] M. H. Ittner, U. S. P. 1,951,511, Mar. 20, 1934, to Colgate-Palmolive-Peet Co.; *Chem. Abs.*, 1934, **28**, 3610; *Brit. Chem. Abs.* **B**, 1935, 109. See also British P. 423,279, 1935; *Chem. Abs.*, 1935, **29**, 4614; *Brit. Chem. Abs.* **B**, 1935, 319.

[48] V. Varlamov, G. Oyat'eva and N. Davuidova, *Masloboino-Zhirovoe Delo,* 1935, 11, 494; *Chem. Abs.*, 1936, **30**, 1215.

On the other hand, the oxidized and unoxidized portions can be separated by selective solvents. Peukert[50] extracted oxidized paraffin wax with ten parts of methyl alcohol in the cold and in this manner removed the greater part of the oxidized material. He also found pyridine to be a useful extraction medium. Beck and associates[51] purified aqueous crude wax-acid soaps by heating them to the melting points of the corresponding anhydrous soaps and then removing the volatile constituents by reducing the pressure. This treatment gave the anhydrous soaps which were almost free of volatile substances of high boiling points. The soaps were then removed in this form or were redissolved in water to give solutions of the desired strength. Pungs and Behringer[52] separated high-molecular weight alcohols from high-molecular weight acids by fractionally distilling mixtures of these under reduced pressures with the aid of steam or the vapor of an organic liquid such as ethyl alcohol or benzene. These mixtures include natural waxes and oxidation products of paraffins. For example, crude montan wax is treated with superheated steam at 200°C. under 60 mm. pressure. The esters present are split up and during a period of 5 hours 20 per cent of the original material distils over and is collected as a slightly yellow solid melting at 78° to 79°C. This is composed of high-molecular weight alcohols having an acetyl number of 120.

The removal of oxidized from unoxidized products of paraffin wax has also been effected by means of liquid sulphur dioxide, acetic acid, ammonia, and other substances.[53] Vesterdal[54] observed that the hydroxy acids could be separated from the fatty acids produced in wax oxidation by the use of phosphoric acid. This investigator states that if concentrated phosphoric acid is agitated with a considerably greater volume of the crude acids, and allowed to stand, separation takes place. The phosphoric acid and hydroxy acids form a lower layer, while the fatty acids form a second layer which may be separated.

STRUCTURE OF WAX ACIDS

As yet, the exact steps occurring in the oxidation of paraffin wax or the structure of the acids thereby obtained are not clearly understood. This is probably due, in large part, to the fact that considerable disagreement exists as to the exact structures of the hydrocarbons comprising the wax. For instance, Marcusson[55] concluded that ordinary paraffin wax consists only of normal aliphatic hydrocarbons, whereas Gränacher[56] expressed a belief that it contains principally branched-chain hydrocarbons. On the other hand, by successive crystallizations of petroleum asphalt from pyridine and ether, and finally from benzene, Müller and Pilat[57] separated the bulk of the paraffin wax into four fractions which contained both true paraffins and some cyclic hydrocarbons. X-Ray studies[58] on white paraffin wax have indicated the presence of saturated cycloparaffins and branched-chain paraffins.

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[49] V. Varlamov and Z. Kenigsberg, *Masloboino-Zhirovoe Delo*, 1935, 11, 203; *Chem. Abs.*, 1935, **29**, 7629.

[50] E. Peukert, U. S. P. 1,987,208, Jan. 8, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 1430.

[51] C. Beck, H. Weissbach and H. Diekmann, U. S. P. 1,965,566, July 10, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5697.

[52] W. Pungs and K. Behringer, German, P. 583,323, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.* 1934, **28**, 173.

[53] See, Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934. See also R. Heublyum, *Seifensieder-Ztg.*, 1935, **62**, 421, 443; *Chem. Abs.*, 1935, **29**, 4962.

[54] H. G. Vesterdal, U. S. P. 2,038,617, April 28, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 3836.

[55] J. Marcusson, *Chem.-Ztg.*, 1925, **49**, 166; *Chem. Abs.*, 1925, **19**, 3081; *J.S.C.I.*, 1925, **44**, 250B.

[56] C. Gränacher, *Helv. Chim. Acta*, 1920, **3**, 721; *Chem. Abs.*, 1921, **15**, 668.

[57] J. Müller and S. Pilat, *Nature*, 1934, **134**, 459; *Chem. Abs.*, 1934, **28**, 7506; *Brit. Chem. Abs.* **B**, 1934, 996.

[58] Yannaquis, *Ann. combustibles liquides*, 1934, **9**, 295; *Chem. Abs.*, 1934, **28**, 6288.

Shoruigin and Kreshkov[59] separated hydroxy acids from oxidized paraffin wax by precipitation of their cadmium salts. From these they isolated both straight- and branched-chain acids. By treatment with dimethyl sulphate the carboxylic, but not hydroxyl, groups were methylated. Lactonization of a portion of the acids readily occurred. Distillation of the mixed methyl esters effected an increase in the iodine number, thus indicating that some β-hydroxy acids were present. The formulas of the acids isolated corresponded to either $C_nHH_{2n}O_3$ or $C_nH_{2n+2}O_3$, in which n varied from 10 to 32. Comparison of melting points of these acids with those of known structure indicated the former were either highly branched or mixtures of closely related isomers.

Other investigators, however, have reported that oxidation of paraffin wax leads to the formation of fatty acids such as isopalmitic or arachidic, or of acids having an uneven number of carbon atoms.[60]

USES OF WAX ACIDS

As previously mentioned, the largest use is probably in the manufacture of soaps. Such materials exhibit not only detergent properties but also those of emulsifying agents. In the latter capacity they are reported to be more effective than green soap in the preparation of insecticides from petroleum fractions, such as kerosene or gas oil.[61] Ellis[62] has proposed to employ wax acids for making soap powders. One method is to mix the acids with a relatively large quantity of solid alkali, e.g., sodium carbonate, and heat the mixture. Either liquid or solid fractions of the acids, obtained by filtration at any desired temperature or by fractional distillation, may serve as the acidic constituents of the products. The wax acid soaps are said to produce solutions of high foam-forming and washing capacity.[63] The ammonium soaps of the wax acids in particular are recommended as agents in bringing about the separation of oil-water emulsions, although it is said the raw acids or other salts may be employed for this purpose.[64] A semi-fluid detergent reported to be particularly applicable for removing grease and oil has been prepared by dissolving potassium soaps of wax acids in hydronaphtha.[64a] The proportion of soap may vary between 1 per cent and 50 per cent, depending upon the consistency desired in the detergent.

Oxidized paraffin wax may be compounded with lubricating oils, and the acidity of the resulting material reduced by treatment at 120-140°F. with a decolorizing clay.[65] Addition of esters, for example, those from wax acids and isopropyl alcohol, to lubricating oils renders the latter particularly adaptable during the "running in" period of motors.[66] Incorporation of various salts of these acids, such as those of zinc or magnesium[67] and also of lead[68] with lubricants has been suggested. Barth and Corlew[69] state that the wax acids of molecular weight near 400, acid number of 120 or higher may be converted to pour point depressants for use with lubricating oil. The acids are saponified with a five per cent aqueous solution of sodium hydroxide, and the aqueous solution of soaps decanted from unsaponifiable matter. To the soap solution, a slight excess of aluminum nitrate is added, and the resulting insoluble aluminum soaps are then coagulated by heating (to 190°C.). The resulting soaps are washed with water and benzol, and the purified product added to lubricating oil.

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[59] P. P. Shoruigin and A. P. Kreshkov, *J. Gen. Chem.* (*U.S.S.R.*), 1934, 4, 988; *Chem. Abs.*, 1935, 29, 2147.

[60] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[61] B. G. Nemiritzkii, *Bull. Plant Protection* (*U.S.S.R.*), 1931, 3 (1), 201; *Chem. Abs.*, 1933, 27, 5876.

[62] Carleton Ellis, U. S. P. 1,999,184, Apr. 30, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1935, 29, 4198.

[63] H. Franzen, German P. 627,808, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, 30, 6091.

[64] French P. 794,711, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, 30, 5078.

[64a] Carleton Ellis, U. S. P. 2,084,632, June 22, 1937, to Standard I.G. Co.

[65] B. Gallsworthy, Canadian P. 334,390, 1933, to The Texaco Development Corp.; *Chem. Abs.*, 1933, 27, 5531.

[66] French P. 748,512, 1933, to Standard Oil Development Co.; *Chem. Abs.*, 1933, 27, 5531.

A small proportion of alcohols having 8 or more carbon atoms, and derivable from the oxidation products of paraffin wax are of aid in preventing foam in fermentation processes, it has been reported.[70] These alcohols are said to be useful in the preparation of yeast cultures.

The high-molecular weight acids produced by these oxidation processes are said to be useful in making a wave-breaking oil. A mineral oil of low wax content is mixed with high molecular weight organic acids, and the resultant mixture may be used.[71]

Frolich[72] has proposed that the high molecular weight oxygenated products resulting from the oxidation of wax may be cracked to produce lower oxygenated products. Thus, the oxygenated wax products are cracked in the vapor phase at a temperature of 400° to 700°C. in contact with calcium carbonate or ferrous oxide. If temperatures of 600°C. are employed, a contact time of one second is recommended. The high-molecular weight compounds are split in this way to yield a mixture of higher ketones, aldehydes, unsaturated hydrocarbons, pyrones and other oxygenated compounds of lower molecular weight than the feed stock.

Ralston, Pool and Harwood[73] report that wax acids may be reacted with ammonia to form the corresponding aliphatic nitriles. The acids are heated to a temperature somewhat below the boiling point (e.g., about 300°C.) and gaseous ammonia is passed in. The conditions are such that water formed by the reaction is continuously allowed to escape. The course of the reaction, it is suggested, is a primary formation of the ammonium soaps of the acids, followed by a rearrangement with loss of a molecule of water to form an amide. If the water is not permitted to escape, the reaction reaches an equilibrium at this step. However, if a great excess of ammonia is continuously blown through the liquid acids, the water is carried off. The ammonia is recycled, and the water is separated at each cycling. Although the fatty acids tend to decompose at temperatures in the range of 300°C., the investigators report, the presence of the excess of ammonia appears to inhibit this, and the reaction proceeds to give good yields of the nitriles.

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[67] G. H. B. Davis, British P. 401,341, 1932, to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1934, 184; *Chem. Abs.*, 1934, **28**, 2520. Also U. S. P. 2,055,462, Sept. 29, 1936; *Chem. Abs.*, 1936, **30**, 7841.

[68] British P. 434,056, 1934, to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1935, 938.

[69] E. J. Barth and R. P. Corlew, U. S. P. 2,059,192, Nov. 3, 1936, to Sinclair Refining Co.; *Chem. Abs.*, 1937, **31**, 1936.

[70] W. Steibelt, German P. 602,087, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 544.

[71] Dutch P. 67,663, 1933, to Bataafsche Petroleum Maatschappij; *J. Inst. Pet. Tech.*, 1935, **21**, 461A.

[72] P. K. Frolich, U. S. P. 2,068,854, Jan. 26, 1937, to Standard Oil Development Co.

[73] A. W. Ralston, W. O. Pool and J. Harwood, U. S. P. 2,061,314, Nov. 17, 1936, to Armour & Co.; *Chem. Abs.*, 1937, **31**, 710.

Chapter 44

Oxidation from the Standpoint of Detonation

There are two limits of inflammability for each pair of gases (combustible gas and supporter of combustion) forming a combustible mixture. The lower limit corresponds with the minimum proportion and the upper with the maximum proportion of combustible gas conferring inflammability on the mixture. Factors which affect these limits include direction of propagation of the flame, dimensions of the containing vessel and its open or closed condition, turbulence of the gases, and great variations in pressure.[1]

LIMITS OF INFLAMMABILITY OF GASEOUS MIXTURES

Jones, Yant, Miller and Kennedy[2] have determined the limits of inflammability of diethyl ether and ethylene in air and oxygen. For measurement of air mixtures, an upright closed iron cylinder (10.2 x 96.5 cm.) was used. For determinations in an atmosphere of oxygen a glass tube (4.4 x 60 cm.) was employed. The mixtures were ignited by a spark from an induction coil and the flame propagated upward through the tube or cylinder. The values observed for the upper and lower limits of inflammability of diethyl ether in air were 36.50 and 1.85 per cent by volume respectively. The same limits for ethylene-air mixtures were found to be 28.60 and 2.75 per cent by volume respectively. The explosion range of such mixtures as those of carbon disulphide, carbon tetrachloride and air have been determined by Popov and Bezzub.[3] The lower ignition limit for a mixture of air and pure carbon disulphide was found to be 1.7-1.8 per cent, and for a commercial product (79.4 per cent pure) it was 1.19 to 2.1 per cent.

Effect of Pressure. Breton and Laffitte,[4] in measuring the limits and speed of detonation for mixtures of oxygen with propane, butane, acetylene, ammonia and diethyl ether, observed that with increase of pressure the explosive limits were widened. Thus, lower and upper limits of 15 and 90-90.4 per cent by volume were found for hydrogen under 1 atmosphere. With a pressure of 8.7 atmospheres the lower and upper limits were 13.9-14.3 and 91.1-91.3, respectively. It was also noted that the addition of small quantities of hydrogen to a carbon monoxide-oxygen mixture lowered its lower explosion limit and that lead tetraethyl had no appreciable effect on the detonation limits.

Effect of Temperature. The inflammability limits of mixtures of air with isopentane, hexane, heptane, octane, benzene, toluene, cyclohexane and cyclohexene, methanol, ethanol, propanol, acetone, as well as blends of these over the temperature range 100° to 300°C. have been investigated.[5] In the temperature interval 100-250°C. the upper and lower limits for benzene were found to be 17.9 and 4.9 per cent, respectively, while for toluene they were 27.0 and 3.0 per cent. The lower limit of inflammation was linear with reference to temperature for both hydrocarbons. The upper limit, on the other hand, for benzene obeyed the same law, but above 200°C. the values for toluene were distinctly lower than would correspond to linear variation. This was explained by the formation of an oxidation product in the case of toluene, which with the unoxidized aromatic gave rise to a mixture having an upper limit lower than that of pure toluene. Although the lower limits as determined for cyclohexane and cyclohexene were close together, the difference in the upper limits was more marked. At 150°C., a mixture of air and ethanol containing 80.5 per cent water vapor still propagated flame.

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[1] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. A report of the ignition range of mixtures of hydrogen, carbon monoxide, methane, ethane and homologues, benzene, toluene, ethylene, propene, acetylene, pyridine, in air and oxygen can be obtained from the investigations of A. Pignot, *J. usines gaz.*, 1935, **59**, 118; *Chem. Abs.*, 1935, **29**, 6022. This work includes curves and tables for the ignition ranges of the pure gas-air mixtures studied, and for some ternary and technical gas mixtures.

[2] G. W. Jones, W. P. Yant, W. E. Miller, and R. E. Kennedy, *Bur. Mines Rept. of Investigations* No. 3278, 1935; *Chem. Abs.*, 1935, **29**, 7078; *Brit. Chem. Abs.* **A**, 1935, 1206.

[3] P. V. Popov and K. E. Bezzub, *Trans. Sci. Inst. Fertilizers and Insectofungicides, U.S.S.R.* No. 123, 1935, 210; *Chem. Abs.*, 1936, **30**, 3649.

[4] J. Breton and P. Laffitte, *Compt. rend.*, 1936, **202**, 316; *Chem. Abs.*, 1936, **30**, 2003; *Brit. Chem. Abs.* **A**, 1936, 432.

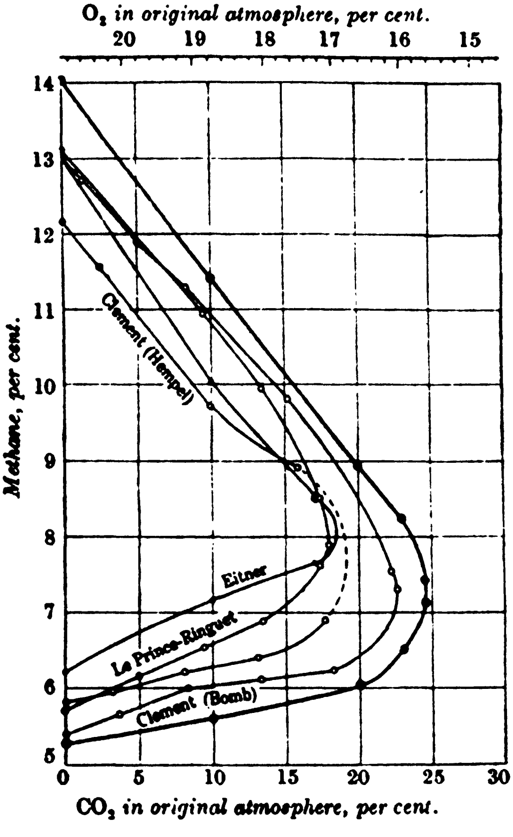

FIG. 219.
Influence of Carbon Dioxide on Inflammability Limits of Methane-Air Mixtures. (H. F. Coward and F. J. Hartwell)

Courtesy Journal of the Chemical Society

In 1891, Le Chatelier stated that a mixture of any two limit mixtures (both upper or both lower) will itself be a limit mixture. Briand[6] tested this rule upon binary and ternary vapor-air mixtures, namely ethanol and cyclohexane, ethanol-benzene, benzene and cyclohexene, ethanol-methanol-benzene, and ethanol-benzene-cyclohexane. Although only the lower limit concentrations of these mixtures were determined, the accord between the calculated and found values was good.

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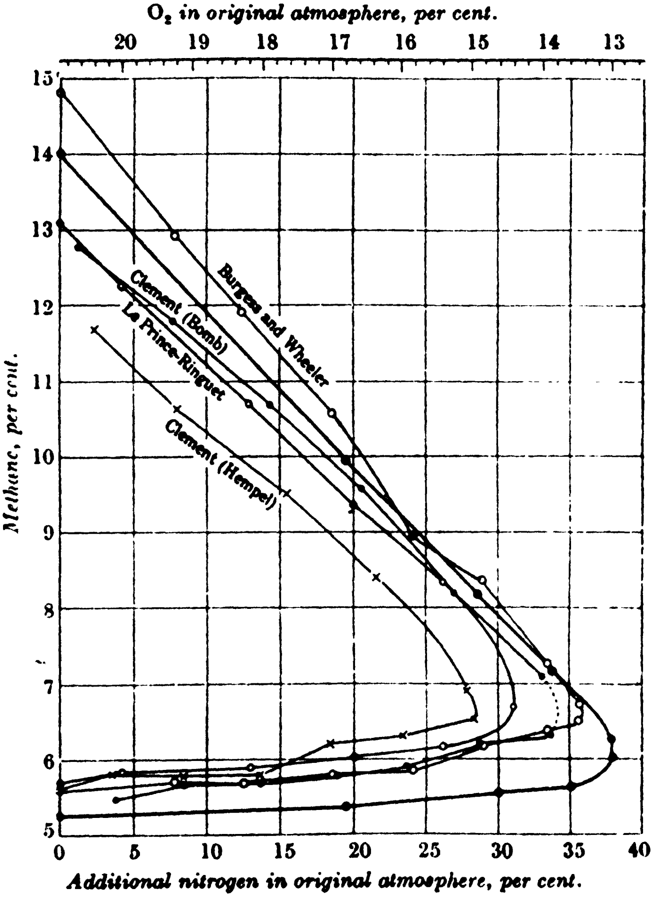
[5] M. Briand, *Ann. combustibles liquides*, 1935, **10**, 1129; *Chem. Abs.*, 1936, **30**, 1563; *Brit. Chem. Abs.* **B**, 1936, 728; *J. Inst. Pet. Tech.*, 1936, **22**, 109A. See also M. B. Neiman and V. O. Estrovich, *J. Phys. Chem.* (*U.S.S.R.*), 1935, **6**, 445; *Chem Abs.*, 1936, **30**, 2064.

[6] M. Briand, *loc. cit.*



Courtesy Journal of the Chemical Society

FIG. 220.—Effect of Nitrogen on Inflammability Limits of Methane-Air Mixtures. (H. F. Coward and F. J. Hartwell)

Effect of Flame Propagation. The effect of the direction of flame propagation on the limits of inflammability of hydrogen and deuterium is discussed by Payman and Titman.[7] The lower limits for both hydrogen and deuterium in air and oxygen (with a tube 2.2 x 45 cm.), using upward propagation of flame, were 3.9 and 4.9 per cent, respectively. With downward propagation under the same conditions the lower limits were found to be 9.1 and 10.2 per cent for hydrogen and deuterium, respectively. However, the upper limits were the same irrespective of the direction of propagation of flame, being 94.2 and 73.0 per cent for hydrogen in oxygen and air, respectively. Values for deuterium were 94.7 per cent with oxygen and 75.0 per cent with air.

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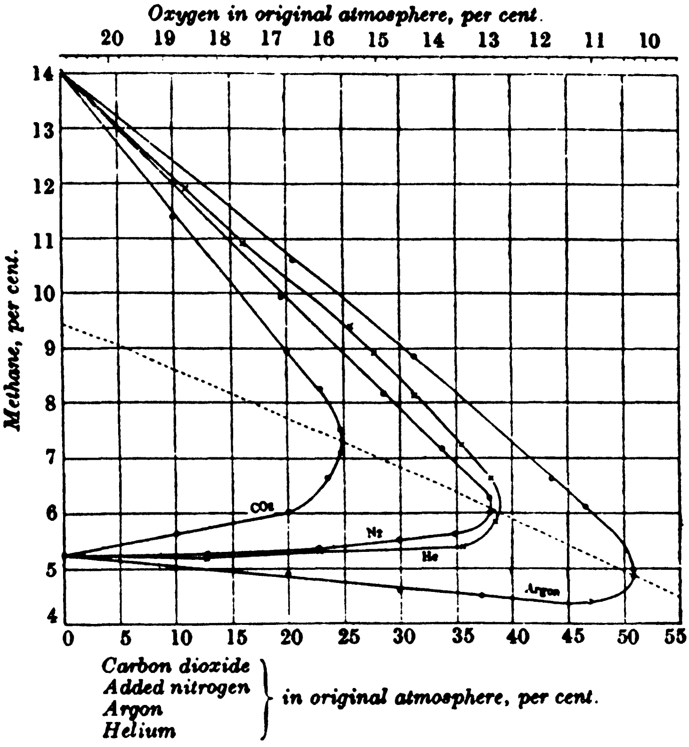
[7] W. Payman and H. Titman, *Nature*, 1936, 137, 190; *Chem. Abs.*, 1936, 30, 2816; *Brit. Chem. Abs.* A, 1936, 431.

Effect of Inert Gases. The influence of inert gases on the extinction of methane flames has been investigated by Coward and Hartwell.[8] In methane-air mixtures, carbon dioxide narrowed the limits of inflammability as the proportion of diluent was increased. This is shown graphically in Fig. 219. The heavy curve represents the limits (upper and lower) of inflammability of methane in atmospheres composed of air admixed with the indicated proportions of carbon dioxide. As the amount of diluent gas is increased, the limits narrow until they meet when the atmosphere contains somewhat less than 25 per cent of carbon dioxide. The increase in the lower limit was attributed to the greater thermal capacity of the carbon dioxide, and this cause, together with the reduction in oxygen content of the atmosphere were considered responsible for the decrease in the upper limit.



Courtesy Journal of the Chemical Society

FIG. 221.—Influence of Inert Gases on Inflammability Limits of Methane-Air Mixtures. (H. F. Coward and F. J. Hartwell)

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[8] H. F. Coward and F. J. Hartwell, *J.C.S.*, **1926**, 1522; *Chem. Abs.*, 1926, **20**, 3573; *Brit. Chem. Abs.* **A**, 1926, 805. See also G. W. Jones and R. E. Kennedy, *Ind. Eng. Chem.*, 1935, **27**, 1344; *Chem. Abs.*, 1936, **30**, 289; *Brit. Chem. Abs.* **B**, 1936, 177; *J. Inst. Pet. Tech.*, 1936, **22**, 22A.

In the same graph are indicated the results obtained by Eitner,[9] Clement,[10] and Leprince-Ringuet.[11] These results are not strictly comparable, however, for the experimental conditions were somewhat different in each case.

In Fig. 220 the heavy curve represents (as above) the inflammability limits of methane in atmospheres composed of air admixed with the indicated amounts of nitrogen. This figure also includes some values reported by Clement,[12] Leprince-Ringuet,[13] and Burgess and Wheeler.[14] As in the case of carbon dioxide, these data are not strictly comparable, due to differences in experimental procedure. The influence of argon and helium on the limits of inflammability of methane-air mixtures was also investigated. It was concluded that in the methane-air-argon mixtures the lower limit of methane will have smaller values, since argon has a lower heat capacity than air. These facts are indicated by the data shown graphically in Fig. 221. Since the heat capacity of helium is very nearly equal to that of argon, it was thought that these gases should be somewhat alike in their effect as diluents. Fig. 221 shows helium to be markedly more extinctive of methane-air flames than argon. In summarizing the results of the above work, it was stated that the diluent gases affect the inflammability limits of methane-air mixtures by reducing the oxygen content of the mixture, its thermal capacity or its thermal conductivity. The thermal capacity effect is marked in the case of argon, for the lower limit of methane, under conditions described, is reduced from 5.24 per cent in air to 4.40 per cent in an atmosphere composed of 47 per cent of argon and 53 per cent of air.

Jones and Kennedy[15] made a study of the effect of varying proportions of nitrogen and carbon dioxide on the inflammability limits of mixtures of methane, ethane, propane, and butane. Some of the results are given in Table 193. Fig. 222 represents graphically the influence of these inert gases on the values for propane. As the proportion of carbon dioxide increases both limits are raised until they narrow and meet when a ratio of diluent to hydrocarbon of about 8 to 1 is reached. Like-

TABLE 193.—*Limits of Inflammability of Methane, Ethane, Nitrogen, and Carbon Dioxide Mixtures.*

Composition of Original Mixture Air-free Basis, Per cent by Volume		Mixtures Divided into Two Component Mixtures as Follows		Ratio of Nitrogen or Carbon Dioxide to Combustible	Total Per cent of Components	Inflammability Limits	
						Lower	Upper
Methane	40.6	Methane Carbon Dioxide	40.6 24.2	0.60	64.8	8.5	19.0
Ethane	7.6						
Carbon Dioxide	24.2						
Nitrogen	27.6	Ethane Nitrogen	7.6 27.6	3.63	35.2	14.6	32.1
Total	100.0		100.0		100.0		
		Methane Nitrogen	40.6 27.6	0.68	68.2	8.4	20.8
		Ethane Carbon Dioxide	7.6 24.2	3.18	31.8	13.6	27.9

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[9] P. Eitner, *Habilitationsschrift, München*, 1902.

[10] J. K. Clement, *U. S. Bureau of Mines, Technical Paper* 43, 1913.

[11] F. Leprince-Ringuet, *Compt. rend.*, 1914, 158, 1999.

[12] J. K. Clement, *loc. cit.*

[13] F. Leprince-Ringuet, *loc. cit.*

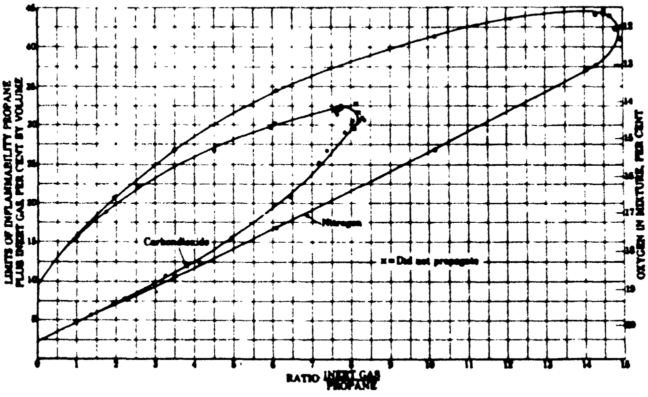
[14] M. J. Burgess and R. V. Wheeler, *J.C.S.*, 1914, 105, 2596.

[15] G. W. Jones and R. E. Kennedy, *Bur. Mines Rept. of Investigations* 3216, 1933; *Chem. Abs.*, 1933, 27, 4057; *Gas Age-Record*, 1933, 72, 53; *Chem. Abs.*, 1934, 28, 287.

wise, when nitrogen is employed the limits meet when a ratio of nearly 15 to 1 is attained. Behavior of the inert gases in the case of butane is similarly shown in Fig. 223.

Van Heiningen[16] concluded that the extinguishing action of inert gases decreases in the order: carbon dioxide, helium, nitrogen and argon, regardless of the nature of the explosive gas. Also that the upper explosion limits are mainly affected but the lower ones are little changed by the nature or amount of diluent added.

The influence of inorganic dusts on binary mixtures of air with various combustible gases was investigated by Thompson.[17] The presence of magnesium oxide dust narrowed the explosion range at both ends. With ethylene mixtures this effect was more marked than with those of hydrogen or carbon monoxide. In the case of benzene and diethyl ether the effect was barely perceptible and with methane it was absent. Substitution of silica dust for magnesium oxide dust gave comparable results. With iron carbonyl vapor it was noted that a greater displacement (of explosion range) was effected than with magnesium oxide, but whether the effects were due to the undecomposed carbonyl molecules or to the iron (or oxide) formed by their decomposition was uncertain. An explanation proposed for the action of mineral dusts was that radicals or atoms, i.e., hydroxyl radicals or hydrogen atoms, propagating the reaction chains were absorbed and converted into stable molecules.



Courtesy U. S. Bureau of Mines

FIG. 222.—Effect of Nitrogen and of Carbon Dioxide on Inflammability Limits of Propane. (G. W. Jones and R. E. Kennedy)

Jones and Kennedy[18] determined the amount of carbon tetrachloride that must be added to pentane, hexane, heptane, octane, or gasoline to render the resulting mixtures non-flammable. Determinations of the inflammability limits of such liquid blends were complicated by the differences in boiling points and vapor pressures of the chlorinated compound and the hydrocarbons. Under conditions of complete vaporization in an explosion tube the following percentages of tetrachloride were required to prevent flame propagation: pentane, 66.7; hexane, 70; heptane, 70; octane, 66.7; naphtha (boiling range 97-155°C.) 70; and gasoline (boiling range 31-205°C.) 58.0.

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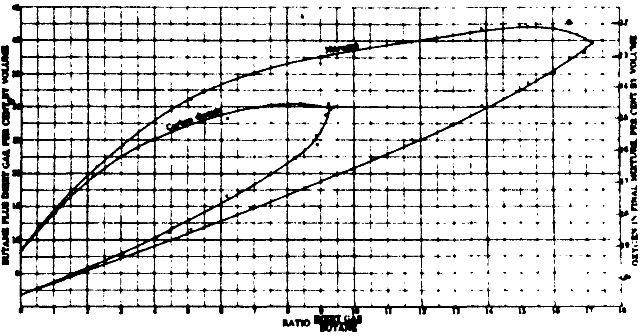
[16] J. van Heiningen, *Rec. trav. chim.*, 1936, **55**, 65; *Chem. Abs.*, 1936, **30**, 3237; *Brit. Chem. Abs.* **A**, 1936, 431.

[17] H. W. Thompson, *Z. physik. Chem.*, 1932, **18B**, 219; *Brit. Chem. Abs.* **A**, 1932, 1001.

[18] G. W. Jones and R. E. Kennedy, *Bur. of Mines, Information Circ.* No. 6805, **1934**; *J. Inst. Pet. Tech.*, 1935, **21**, 181A; *Chem. Abs.*, 1935, **29**, 1985.

Ignition of Gases by Heated Surfaces

The exposure of inflammable mixtures to heated surfaces has been one of the most popular methods of determining ignition temperatures. The results thus obtained do not give absolute values since they are influenced by other factors, e.g., the nature and extent of the igniting surface.[19] Investigations carried out on the effect of different types of surfaces on the lower explosion limits of methane-oxygen mixtures,[20] revealed that when a quartz vessel, whose surface had been treated with hydrofluoric acid, was used in the temperature range of 602° to 642°C. the induction period of the explosion was reduced to about 3 minutes. Extent of acid treatment of the vessel surface affected the lower limit pressure of the gas mixtures. Thus, the value was 33.5 to 38.5 mm. after a 20 minute treatment and 18.0 to 22.0 mm. when the vessel had been exposed 150 minutes. The age of the surface treated also influenced the results.



Courtesy U. S. Bureau of Mines

Fig. 223.—Influence of Nitrogen and of Carbon Dioxide on Inflammability Limits of Butane. (G. W. Jones and R. E. Kennedy)

Other types of surface treatments studied were the deposition of a silver mirror on the inside of the vessel, the quartz surface rinsed from 1*M* potassium chloride, and lastly the quartz surface rinsed with 1*M* aluminum nitrate. In the temperature range previously mentioned and at a pressure interval of 25 to 60 mm. the silver surface did not induce any explosions of a mixture of 1 volume of methane to 2.4 volumes of oxygen. However, the reaction rate was considerably slower than with the hydrofluoric acid-treated quartz. Under the same conditions the potassium chloride-treated surface did not induce any explosion up to 110 mm. pressure, the reaction being greater than, but of the same order as, that in hydrofluoric acid-treated quartz. With the alumina-coated surface explosions did occur in about the same pressure and temperature ranges as the hydrofluoric acid-treated quartz. but the surface aged more rapidly, until, after 24 hours no explosion could be obtained. The conclusion was made that, in the investigation of ignition temperatures of gases and gaseous mixtures by heated surfaces, if reproducible results are desired one should use a surface which can be accurately duplicated and will not age rapidly.

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[19] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[20] H. H. Storch, *J.A.C.S.*, 1935, **57**, 685; *Chem. Abs.*, 1935, **29**, 3517; *Brit. Chem. Abs.* **A**, 1935, 709; *J. Inst. Pet. Tech.*, 1935, **21**, 160A. The mechanism of the upper limit of ignition of a mixture of ethane and oxygen has been reported by P. Sadovnikov, *Physik Z. Sowjetunion*, 1933, **4**, 743; *Chem. Abs.*, 1934, **28**, 2979. For the derivation of an equation for the period of induction in the inflammation of gas mixtures see A. E. Malinovskii, *Acta Physicochim. (U.S.S.R.)*, 1935, **3**, 509; *Chem. Abs.*, 1936, **30**, 2387. The induction time and ignition temperature of methane-hydrogen mixtures has been discussed by H. Sachsse, *Z. Elektrochem.*, 1936, **42**, 504; *Chem. Abs.*, 1936, **30**, 6945.

DETERMINATION OF IGNITION TEMPERATURES

These determinations have long been a subject of controversy, due to the many different values obtained through the use of widely variant methods and apparatus. Dixon's work[21] on the ignition points of gaseous mixtures using a "concentric tube" apparatus, under varying conditions of pressure and time lag has been compiled by Coward.[22] Dixon's apparatus consists essentially of a glazed silica cylinder enclosed within a clay tube, the latter being wound with nichrome wire which is used for heating. Air or oxygen is admitted through the larger of two concentric tubes at the base of a silica cylinder, while the inner or smaller tube which extends to the center of the cylinder carries the gas to be studied. The burnt gases are removed at the top of the cylinder. All of the equipment is well insulated against heat losses and built to withstand high pressures.

The investigations included the mixtures: hydrogen-air (dry and also containing 5.3 per cent water vapor), hydrogen-oxygen, carbon monoxide-air (moist), carbon monoxide-hydrogen (varying concentrations of hydrogen in moist and dry air), carbon monoxide-oxygen (dry and moist). Results were also obtained for mixtures of methane, ethane, pentane, benzene, and of ethylene with either air or oxygen.

In Tables 194 and 195 are listed the rapid-ignition points, at atmospheric pressure, of some of the gases studied. These points, i.e., rapid ignition points, may be defined as the minimum temperature to which a gas and the atmosphere must be raised, prior to admixture, so that the gas inflames 0.5 second after opening the jet. The values are usually higher than the minimum temperature required to ignite such a mixture when it flows continuously from a jet. The latter are designated as ignition points of stream.

TABLE 194.—*Ignition Points of Various Gases.*

	In Oxygen		In Air	
Gas	Rapid-Ignition Point, °C.	Ignition Point of Stream, °C.	Rapid-Ignition Point, °C.	Ignition Point of Stream, °C.
Hydrogen	625	585	630	585
Carbon monoxide	687[a] 680[b]	650[c]	693[a] 683[b]	651[c]
Cyanogen	—	811	—	856
Carbon disulphide	132	—	156	—
Hydrogen sulphide	—	227	—	364
Ammonia	—	700-860	—	—
Diethyl ether	219	—	549	—

[a] 0.63 per cent water in atmosphere.
[b] 5.3 per cent water in atmosphere.
[c] 2.0 per cent water in gas and in atmosphere.

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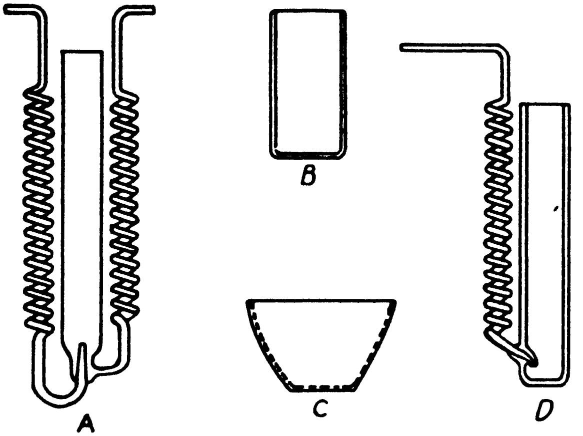
[21] Investigations of H. B. Dixon for Safety in Mines Research Board, Sheffield. England.

[22] H. F. Coward, *J.C.S.*, 1934, 1382; *Chem. Abs.*, 1935, 29, 655; *Brit. Chem. Abs.* A, 1934, 1178; *J. Inst. Pet. Tech.*, 1934, 20, 564A. For a discussion of the relationship between spontaneous ignition temperature and anti-detonation quality see I. R. Roseanu. *Mon. petrole roumain*, 1936, 37, 1021; *J. Inst. Pet. Tech.*, 1936, 22, 467A.

TABLE 195.—*Ignition Points of Hydrocarbons.*

	In Oxygen		In Air	
Gas	Rapid-Ignition Point, °C.	Ignition Point of Stream, °C.	Rapid-Ignition Point, °C.	Ignition Point of Stream, °C.
Methane	664	556-700	722	650-750
Ethane	628	520-630	650	520-630
Propane	—	490-570	—	—
Pentane	355	—	600	—
Ethylene	604	510	627	543
Propene	586	—	618	—
Acetylene	—	428	435	429
Benzene	685	—	710	—

The ignition temperatures tabulated show that inflammation of the various gases takes place at a lower temperature in oxygen than in air for the same pressure. In the cases of hydrogen and of carbon monoxide ignition temperatures were increased only 3° to 6°C. with the change in media from oxygen to air. With pentane the difference is 245°C. and for diethyl ether vapor, 330°C.



A. Concentric tube apparatus
B. Pyrex tube
C. Porcelain crucible
D. Pyrex tube with air or oxygen inlet

Courtesy U. S. Bureau of Mines

FIG. 224.—Types of Vessels Employed for Determination of Ignition Temperatures. (G. W. Jones, W. P. Yant, W. E. Miller and R. E. Kennedy)

A similar study has been made by Bunte and Bloch,[23] who found that for a particular gas-air mixture the lowest ignition temperature occurred not with the amount of air required for complete combustion, but rather with a mixture showing the highest reaction velocity in accordance with the mass law. Here again when oxygen was substituted for air the values of the lowest ignition temperature fell considerably.

The flash points of mixtures of methanol (anhydrous) and ethanol (99.5 per cent) with benzine have been recorded by Roberti.[24] With methanol, the flash point was said to be 9.5°C., with ethanol, 14°C.

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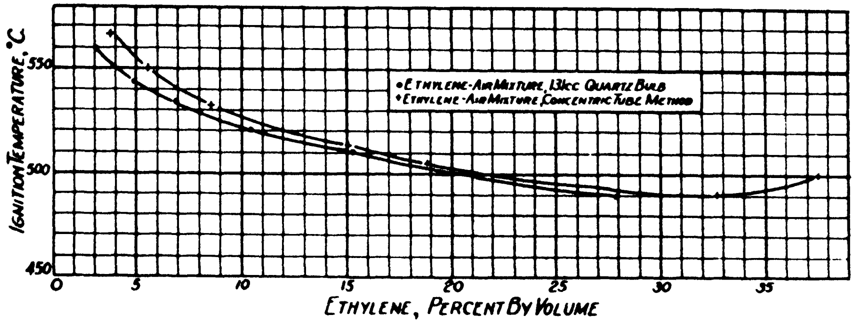
[23] K. Bunte and A. Bloch, *Gas u. Wasserfach*, 1935, **78**, 325, 348, 537, 560; *Brit. Chem. Abs.* **B**, 1935, 660, 933; *Chem. Abs.*, 1935, **29**, 6731.

[24] G. Roberti, *Ricerca sci.*, 1934, **5** (2), 8; *Brit. Chem. Abs.* **B**, 1935, 791; *Chem. Abs.*, 1935, **29**, 5625.

EFFECT OF CONCENTRATION OF CERTAIN SUBSTANCES ON IGNITION TEMPERATURES

Jones[25] and co-workers investigated the ignition points of diethyl ether admixed with air or oxygen. Using the drop method apparatus (shown in Fig. 224, design D) the minimum ignition temperature was 182°C. in oxygen. With the apparatus of design B the minimum inflammation temperature in air was 304°C. Mixtures of diethyl ether vapor (containing 3.5 per cent by volume ethyl alcohol) showed higher ignition values in air in all vessels, i.e., in vessels of design B, C, D in Fig. 224, the temperatures in air were 317°, 334° and 387°C., respectively. The minimum inflammation temperatures for ethylene-air mixtures in which the concentration of ethylene varied between 3 and 38 per cent by volume, were determined in the concentric tube apparatus shown in Fig. 224, design A. Results are presented graphically in Fig. 225. Bunte and Bloch[26] noted that high hydrocarbon concentration caused higher ignition temperatures.[27]



Courtesy U. S. Bureau of Mines

FIG. 225.—Ignition Temperatures of Ethylene-Air Mixtures. (G. W. Jones, W. P. Yant, W. E. Miller and R. E. Kennedy)

Work by Naylor and Wheeler[28] with mixtures of ethane, propane, ethylene and air showed that formaldehyde and ethylene are formed during the lag period for ethane-air mixtures. However, the prior addition of the aldehyde to inflammable mixtures did not shorten the lag. The rate of reaction was thought to be affected more by the concentration of the hydrocarbon than by the proportion of oxygen in the mixture. Also, it was noted that the ignition temperatures decreased with increase of molecular weight of the hydrocarbon. Low rates of reaction in the case of propene were explained on the basis of steric hindrance. Dykstra and Edgar,[29] using a concentric tube apparatus similar to that employed by Dixon,[30] determined the spontaneous ignition temperatures of gasoline vapor-oxygen mixtures. For a given mixture the ignition temperatures were lowered smoothly as the oxygen to fuel ratio was increased until suddenly an abrupt drop of about 200°C. occurred with only a small change in the ratio as shown in Fig. 226. Similar abrupt changes took place in the ignition temperature also when small variations were made in the percentage of gasoline vapor in the inner tube, with the oxygen to fuel ratio constant, as shown in Fig. 227.

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[25] G. W. Jones, W. P. Yant, W. E. Miller and R. E. Kennedy, *Bur. Mines, Rept. of Investigations* No. 3284, **1935**; *Brit. Chem. Abs.* **A**, 1935, 1327; *Chem. Abs.*, 1935, **29**, 7041.

[26] K. Bunte and A. Bloch, *loc. cit.*

[27] Inflammation temperatures of divinyl ether-air or oxygen mixtures and ether-ethanol-oxygen mixtures are given by G. W. Jones and B. B. Beattie, *Ind. Eng. Chem.*, 1934, **26**, 557; *Chem. Abs.*, 1934, **28**, 3903; *Brit. Chem. Abs.* **B**, 1934, 568.

[28] C. A. Naylor and R. V. Wheeler, *J.C.S.*, **1933**, 1240; *Chem. Abs.*, 1934, **28**, 327; *Brit. Chem. Abs.* **A**, 1933, 1123.

[29] F. J. Dykstra and G. Edgar, *Ind. Eng. Chem.*, 1934, **26**, 509; *Brit. Chem. Abs.* **B**, 1934, 563; *J. Inst. Pet. Tech.*, 1934, **20**, 404A; *Chem. Abs.*, 1934, **28**, 3903.

[30] H. B. Dixon and H. F. Coward, *J.C.S.*, 1909, **95**, 514; *J.S.C.I.*, 1909, **28**, 301; *Chem. Abs.*, **1909**, **3**, 1343.

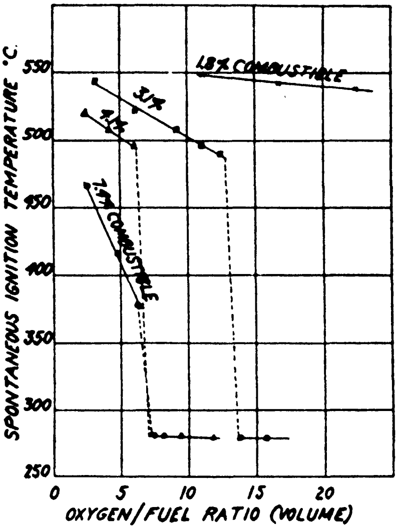

Fig. 226.
Spontaneous Ignition Temperature of Gasoline as Affected by Oxygen to Fuel Ratio. (F. J. Dykstra and G. Edgar)

Courtesy Industrial and Engineering Chemistry

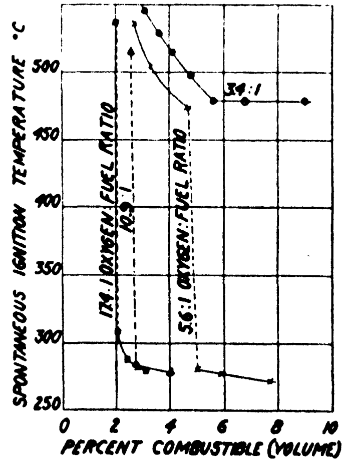

Fig. 227.
Effect of Fuel Vapor Concentration on Spontaneous Ignition Temperature of Gasoline. Constant Oxygen to Fuel Ratio. (F. J. Dykstra and G. Edgar)

Courtesy Industrial and Engineering Chemistry

These observers noted, using a different technique, that certain gasolines possess two distinct ignition temperatures at definite concentrations and oxygen to fuel ratio. For example, with a mixture containing 4.6 per cent gasoline vapor by volume and having an oxygen to fuel ratio of 8.2 to 1, ignition was first noted at a temperature of 280°C. as shown in Fig. 228. As the temperature was allowed to rise, inflammation occurred at short intervals until the mixture reached 314°C., at which point ignition ceased. At 444°C., inflammation commenced again, but the explosions were somewhat less violent than those in the range 280° to 314°C.

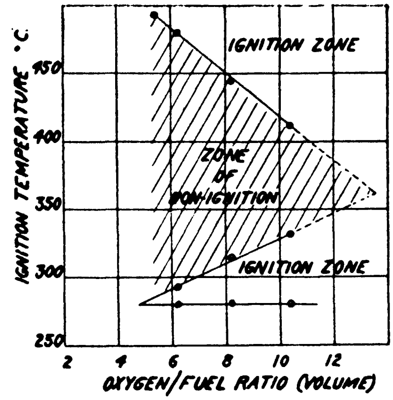

FIG. 228.
Zones of Ignition and Non-ignition for Gasoline. (F. J. Dykstra and G. Edgar)

Courtesy Industrial and Engineering Chemistry

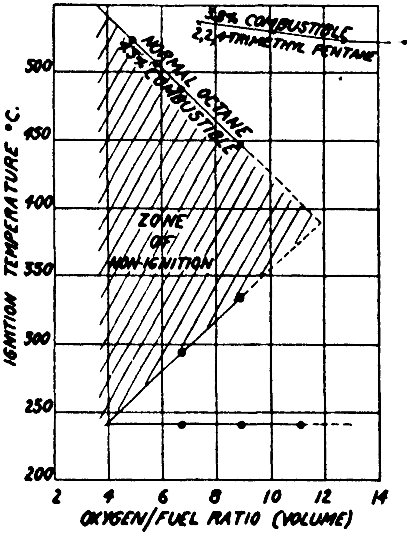

FIG. 229.
Ignition Characteristics of *n*-Octane and of Isooctane (2,2,4-Trimethylpentane). (F. J. Dykstra and G. Edgar)

Courtesy Industrial and Engineering Chemistry

These same zones of ignition and non-ignition were passed through by lowering the temperature slowly. Fig. 229 illustrates similar results obtained with two pure isomeric hydrocarbons, namely *n*-octane and 2,2,4-trimethylpentane. *n*-Octane shows zones of ignition and non-inflammability similar to those obtained for gasoline (previously discussed). A 3.8 per cent fuel vapor mixture of 2,2,4-trimethylpentane showed no ignition temperature below 523°C. and a relatively slight effect of oxygen-to-fuel ratio. The lowered temperature limit was not affected by changes in concentration of the combustible mixture, but the highest one was very sensitive to small differences. Ignition temperatures in oxygen were found to be less sensitive to variations in conditions than when determined in air.

Experiments[31] have also been carried out, using apparatus akin to that of Bunte and Bloch,[32] to study the relationship between ignition temperature and concentration of a combustible gas for the vapor-air mixtures of propane, butane, pentane, and other hydrocarbon gases. It was found that the lowest ignition temperature for a given mixture always occurred with the combustible vapor in excess and that the temperatures decreased with increasing number of carbon atoms.

EFFECT OF PRESSURE ON IGNITION TEMPERATURES

Townend and co-workers[33] studied the influence of pressure on the spontaneous ignition of mixtures comprising air and butane, pentane, hexane or isobutane. For butane-air mixtures, the ignition temperatures fell into two groups, the one, for determinations below 3 atmospheres pressure and at temperatures greater than 450°C., and the other for greater pressures and temperatures below 370°C. Also with pentane-air mixtures upon which the pressure was less than 3 atmospheres one group (of ignition temperatures) lay above 490°C., and with greater pressure there was a group lying below 350°C. A transference of ignition point from the lower to the higher range occurred at a critical (or transition) pressure dependent on the composition of the mixture. At pressures near the critical value the addition of lead tetraethyl raised the ignition point from the lower to the higher temperature. On the other hand, small additions of acetaldehyde at all pressures greater than one atmosphere produced a transference to the lower range. Further observations showed for hexane-air mixtures two regions of spontaneous ignition, one below 350°C. and the other above 495°C. Also, the pressure necessary to transfer ignition from the lower to the higher group was found to be 0.9 atmosphere for rich mixtures. In a limited pressure range just above the critical transition point, addition of 0.05 per cent lead tetraethyl raised the ignition temperatures from the lower to the higher system, as shown graphically in Fig. 230. When the mild steel lining of the explosion vessel was replaced by one of glass a lowering of the ignition points of about 20° occurred in both the higher and lower ranges. The pressure required to decrease the values, however, was always slightly greater than with the mild steel liner. In the case of isobutane-air mixtures the ignition temperatures were below 370°C. and above 390°C., pictured graphically in Fig. 231. The effect of the addition of 0.05 per cent lead tetraethyl was similar to that previously discussed and is also shown in Fig. 231.

Later investigations[34] have extended this work to include methane, ethane and propane. With the higher paraffins the ignition points lay in two well-defined temperature ranges, whereas with methane or the intermediate products to which it gives rise (on ignition) the values were confined to an upper range even at pressures up to 30 atmospheres. With ethane-air mixtures a lower temperature-ignition

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[31] H. Brückner and M. R. Schöneberger, *Brennstoff-Chem.*, 1935, **16**, 290; *Chem. Abs.*, 1936, **30**, 2003; *Brit. Chem. Abs.* B, 1935, 935; *J. Inst. Pet. Tech.*, 1935, **21**, 399A.

[32] K. Bunte and A. Bloch, *Gas u. Wasserfach*, 1935, **78**, 325, 348; *Brit. Chem. Abs.* B, 1935, 660; *Chem. Abs.*, 1935, **29**, 6731.

[33] D. T. A. Townend and M. R. Mandlekar, *Proc. Roy. Soc.* (*London*), 1933, **A141**, 484, **A143**, 168; *Chem. Abs.*, 1933, **27**, 5189; 1934, **28**, 1191; *Brit. Chem. Abs.* A, 1933, 1016; 1934, 151. D. T. A. Townend, L. L. Cohen and M. R. Mandlekar, *Proc. Roy. Soc.* (*London*), 1934, **A146**, 113; *Chem. Abs.*, 1934, **28**, 7016; *Brit. Chem. Abs.* A, 1934, 1179. M. Prettre, *Ann. combustibles liquides*, 1936, **11**, 669; *Chem. Abs.*, 1936, **30**, 8588; *J. Inst. Pet. Tech.*, 1937, **23**, 33A.

[34] D. T. A. Townend and E. A. C. Chamberlain, *Proc. Roy. Soc.* (*London*), 1936, **A154**, 95; *Chem. Abs.*, 1936, **30**, 4008; *Brit. Chem. Abs.* A, 1936, 801. *Cf.* N. I. Kobozev, Y. S. Kazarnovskii and L. I. Kashtanov, *J. Chem. Ind.* (*Moscow*), 1935, **12**, 1030; *Chem. Abs.*, 1936, **30**, 1188. *Acta Physicochim. U.R.S.S.*, 1935, **3**, 857; *Brit. Chem. Abs.* A, 1936, 1209. A. Sokolik and K. Shcholkin, *Acta Physicochim. U.R.S.S.*, 1934, **1**, 311; *Chem. Abs.*, 1935, **29**, 7141; *Brit. Chem. Abs.* A, 1935, 1080. M. Prettre, *Compt. rend.*, 1936, **203**, 561, 619; *Chem. Abs.*, 1936, **30**, 7978; 1937, **31**, 94.

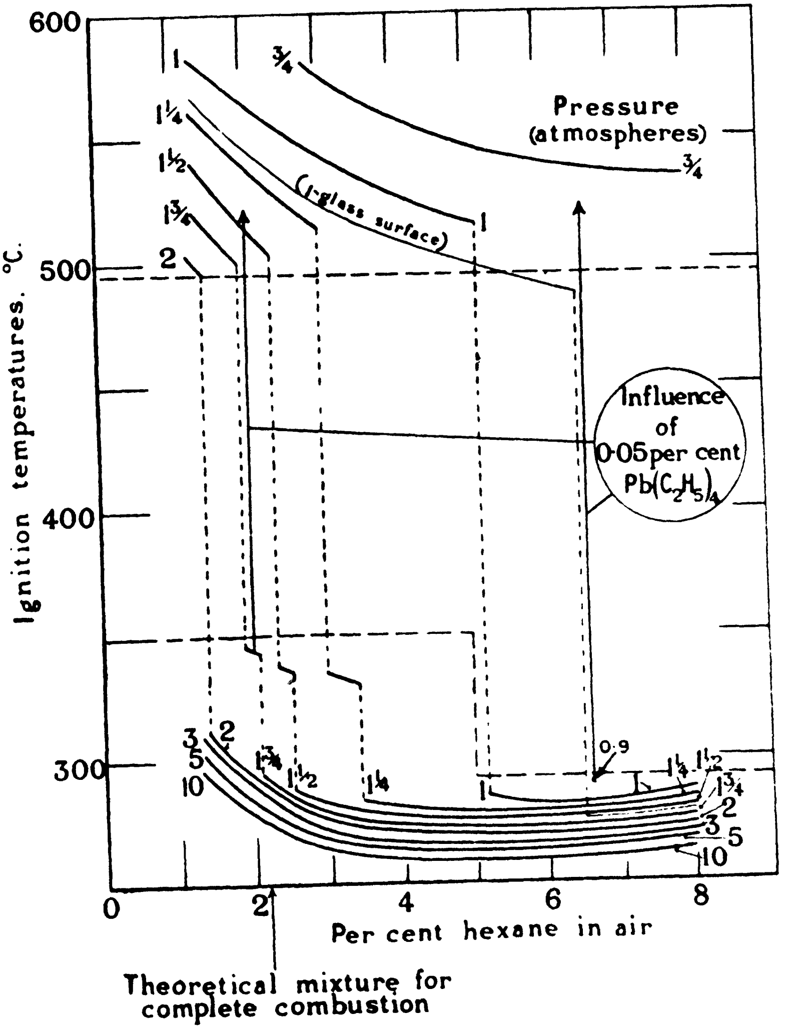

Fig. 230.—Effect of Pressure on Spontaneous Ignition of Hexane-Air Mixtures. (D. T. A. Townend, L. L. Cohen and M. R. Mandlekar)

tion system developed at pressures above 13 atmospheres. The presence of 1 per cent of acetaldehyde in this medium reduced the pressure limit to below 5 atmospheres. Propane-air mixtures revealed all the ignition characteristics of the higher paraffins, ignitions in the lower temperature range being greatly facilitated by the presence of small amounts of either propionaldehyde or acetaldehyde. The investigators concluded that the results further support the theory that the lower group of ignition points occur when the temperature and pressure conditions favor the survival and further oxidation of aldehydes. The higher group of ignition points were believed to result from ignition mainly of the products of thermal decomposition. Also it has been suggested that knock in an engine probably follows a compression ratio promoting ignition in the lower-temperature range. Addition of antiknock compounds raises the pressure necessary for ignition in this range.

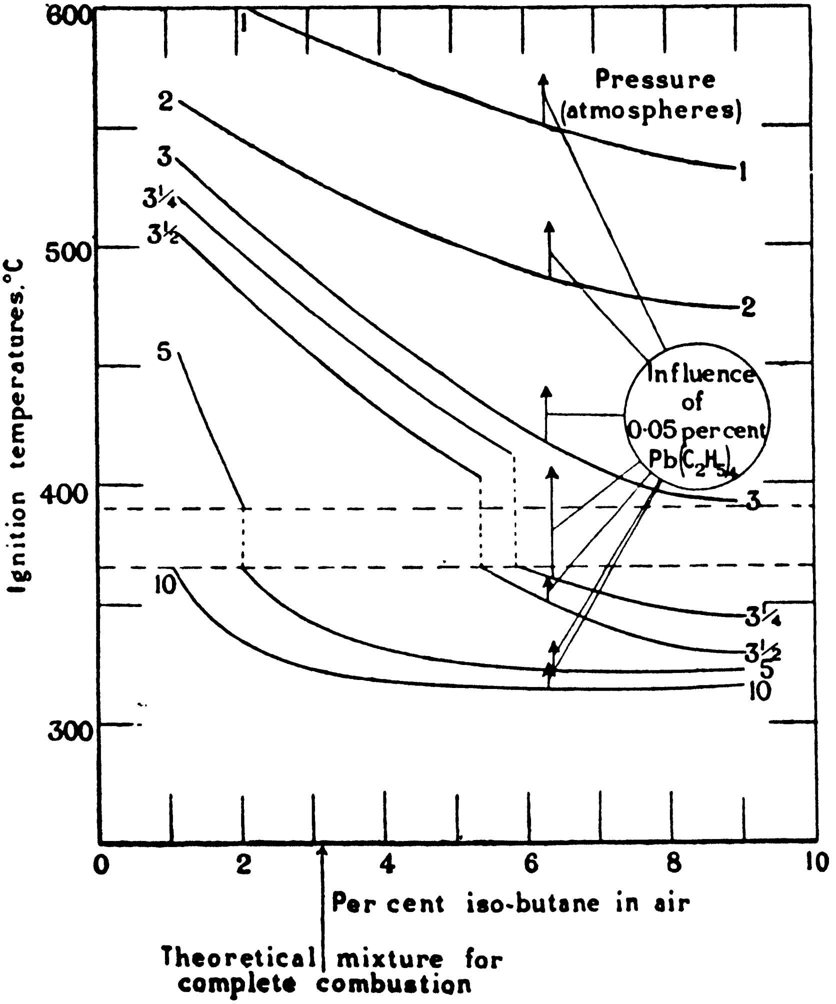

FIG. 231.—Influence of Pressure on Spontaneous Ignition of Isobutane-Air Mixtures. (D. T. A. Townend, L. L. Cohen and M. R. Mandlekar)

Neumann and Aivazov[35] advance another hypothesis which proposes that the velocity of oxidation of the hydrocarbon should increase rapidly with temperature over a wide range of pressure, and should then pass through a maximum into a region of negative temperature coefficients. They suggest that on further raising the temperature the velocity should again increase. Results obtained on the velocity of oxidation of pentane and oxygen in quartz vessels at various pressures below the ignition limit and temperature of 300-500°C. substantiated this theory and also showed two regions of thermal ignition with increasing pressure.

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[35] M. Neumann and B. Aivazov, *Nature*, 1935, 135, 655; *J. Inst. Pet. Tech.*, 1935, 21, 200A; *Chem. Abs.*, 1935, 29, 4586; *Brit. Chem. Abs.* A, 1935, 708. B. Aivazov and M. Neumann, *Z. physik. Chem.*, 1936, B33, 349; *Brit. Chem. Abs.* A, 1936, 1344; *Chem. Abs.*, 1937, 31, 14. *Acta Physicochim. U.R.S.S.*, 1936, 4, 575; *Chem. Abs.*, 1937, 31, 14.

In the study of the condition of spontaneous ignition in mixtures of pentane and oxygen (1 to 8 by volume) at pressures ranging from 5 to 140 cm. Neumann and Estrovich[36] found sharp breaks in ignition temperature in the region of 60 cm. pressure. It was assumed that oxidation proceeds in two ways, that is, at higher pressures ignition is due to the oxidation of an aldehyde or an intermediate oxygenated product. On the other hand, at low pressures, conditions favor thermal decomposition of these bodies to hydrogen, carbon monoxide and methane, which require a higher temperature for ignition. These observations appeared to be closely connected with the greater probability of knocking upon increase of compression in internal combustion engines.

Naylor and Wheeler,[37] from investigations of the ignition of methane-air mixture by a heated surface, propose that the oxidation of methane is a thermal reaction catalyzed by the products of an initial slow and flameless combustion. The explanation, they believe, is not necessarily in conflict with that of chain mechanism set forth by other experimenters who worked with methane and oxygen at lower temperatures. Naylor and Wheeler found that with mixtures containing less than 10.7 per cent methane two pressure limits of ignition exist. For richer mixtures (i.e., more than 10.7 per cent methane) there was only one pressure limit. This was explained on the supposition that at low pressures the lag in ignition increases because of a change in the type of reaction, that is, from surface to gas phase, and also a change in the rate at which different mixtures become non-inflammable as a result of pre-flame combustion.

The influence of pressure on the spontaneous ignition temperatures of gasoline-air mixtures was investigated by Townend and Cohen.[38] They report that in the lower temperature zone there are two types of ignition: one, manifest by slow-travelling bluish flames ("cool flames") which result in small but fairly rapid pressure development and gaseous products rich in bodies strongly aldehydic in character; the second is true ignition manifest by brilliant white light emission accompanied by much greater pressures and explosion products practically free from intermediate oxygenated bodies. Although true ignition in the lower temperature zone is unusual at atmospheric pressure, an increase of pressure soon leads to the development of true ignition which follows the cool flame immediately. In Fig. 232, (curve 1) the data obtained on a rich (6.5 per cent by volume) gasoline-air mixture are presented graphically. Cool flames were observed within the diagonally shaded portion. At pressures below 1.15 atmospheres true ignition occurred in the higher temperature range above 472°C., but at this pressure it was also possible at 342°C.; but not between 342°C. and 472°C. Increase of pressure to 1.45 atmospheres widened the lower inflammation region to between 325° and 360°C. and at the same pressure a second inflammation was initiated at 290°C. Further rise in pressure widened both ranges so that at 1.6 atmospheres ignition occurred between 288° and 308°, between 314° and 364° and finally at all temperatures above 416°C. At pressures greater than 1.9 atmospheres inflammation was possible at all temperatures above 284°C. There are thus two pressure minima of true ignition in the lower temperature range, this type of ignition point curve being characteristic for higher paraffin hydrocarbons.

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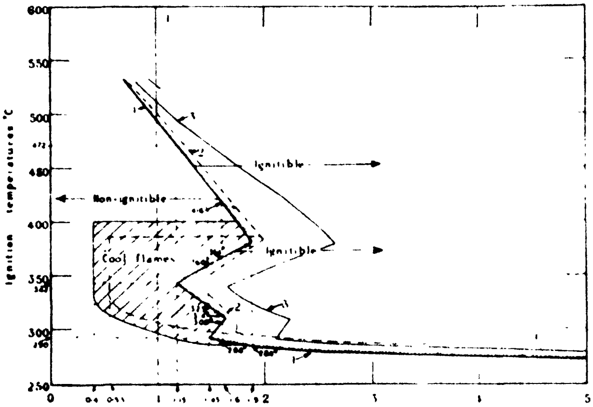
[36] M. Neumann and V. Estrovich, *Nature*, 1934, **133**, 105; *Chem. Abs.*, 1934, **28**, 1903; *Brit. Chem. Abs.* **A**, 1934, 259; *J. Inst. Pet. Tech.*, 1934, **20**, 73A. H. F. Coward (*Nature*, 1934, **133**, 463; *Brit. Chem. Abs.* **A**, 1934, 493; *Chem. Abs.*, 1934, **28**, 6311) reports that pressure-temperature curves for the lag on ignition of pentane vapor heated to a given temperature and issuing into the atmosphere at the same temperature show a break at 60 cm. pressure and are of the same general character as those obtained by Neumann and Estrovich.

[37] C. A. Naylor and R. V. Wheeler, *J.C.S.*, **1935**, 1426; *Chem. Abs.*, 1936, **30**, 2003; *J. Inst. Pet. Tech.*, 1935, **21**, 445A; *Brit. Chem. Abs.* **A**, 1935, 1464. See also N. N. Semenov, *Physik. Z. Sowjetunion*, 1933, **4**, 709; *Chem. Abs.*, 1934, **28**, 2979, for a discussion of considerations pertaining to the theory of the upper pressure limits of ignition.

[38] D. T. A. Townend and L. L. Cohen, *Chem. and Ind.*, **1934**, 267; *Chem. Abs.*, 1934, **28**, 3588; *Brit. Chem. Abs.* **A**, 1934, 603; *J. Inst. Pet. Tech.*, 1934, **20**, 357A.



Courtesy Journal of the Society of Chemical Industry

FIG. 232.—Effect of Pressure on Spontaneous Ignition Temperatures of Gasoline-Air Mixtures. (D. T. A. Townend and L. L. Cohen)

Curve 2 pertains to a mixture of like composition but employing an "ethyl" gasoline and curve 3 is the ignition point curve for a weaker (4 per cent by volume) standard gasoline-air mixture. Townend and Cohen report that knock in an engine is apparently related to a compression rate adequate to allow spontaneous ignition in the lower temperature range, which lies within the ordinary working temperatures of gasoline-air engines. The influence of an antiknock was to increase this compression rate.

Coffey and Birchall[39] observed that a gasoline-air mixture had two spontaneous ignition temperatures (at atmospheric pressure), one "ignition zone" existing from 320°C. to 335°C., then a zone of non-inflammability from 335°C. to 420°C., and finally from 420°C. upward a zone of continuous ignition. With the addition of an antiknock substance, such as aniline, in increasing amounts the lower ignition zone was narrowed until it finally disappeared. When a pro-knock or kerosene was added the lower zone was widened.

EFFECT OF WATER VAPOR ON IGNITION TEMPERATURES

Jones and Seaman[40] investigated the effect of water vapor on the ignition temperature of methane-air mixtures. These experiments were carried out using dry

[39] S. Coffey and T. Birchall. *Chem. and Ind.*, 1934, 245; *Chem. Abs.*, 1934, 28, 3878; *Brit. Chem. Abs.* A, 1934, 603; *J. Inst. Pet. Tech.*, 1934, 20, 234A.

[40] G. W. Jones and H. Seaman, *Ind. Eng. Chem.*, 1934, 26, 71; *Chem. Abs.*, 1934, 28, 1501; *J. Inst. Pet. Tech.*, 1934, 20, 73A; *Brit. Chem. Abs.* A, 1934, 261. See also R. O. King, *J. Inst. Pet. Tech.*, 1934, 20, 791; *J. Inst. Pet. Tech.*, 1934, 20, 565A; *Chem. Abs.*, 1934, 28, 7017; *Brit. Chem. Abs.* A, 1934, 1074. *J. Inst. Pet. Tech.*, 1935, 21, 838; *J. Inst. Pet. Tech.*, 1935, 21, 446A; *Chem. Abs.*, 1936, 30, 289.

gas, also on gases of approximately 20 and 50 per cent relative humidity, and others saturated, at room temperature. The results obtained are listed in Table 196.

TABLE 196.—*Ignition Temperatures of Methane-Air Mixtures.*

Methane, %	Water Vapor Pressure mm. Hg.	Ignition Temp. °C.	Lag on Ignition Seconds	Temp. of Test °C.
4.3	0	650	12	26.0
6.2	0	651	12	27.0
7.9	0	656	11	24.0
9.2	0	660	10	24.0
4.5	0	648	14	25.0
3.9	0	649	13	26.0
4.8	5.0	648	11	24.5
6.25	5.0	651	14	24.5
8.9	5.5	658	9	25.7
4.8	12.4	652	13	26.0
6.5	11.2	654	12	24.3
8.9	10.3	661	9.5	23.0
4.0	25.0	661	11	26.0
5.35	26.5	659	12	27.0
7.6	25.0	661	11	26.0
9.9	22.15	671	8	24.0
11.6	22.15	678	6	24.0
9.6	22.15	668	9	24.0
4.15	22.15	659	10	24.0
4.9	22.15	658	13	24.0
7.2	22.15	659	11	24.9
5.7	22.15	657	11.5	24.0
3.8	22.15	661	10	24.0

The differences between the ignition temperatures for the dry and saturated gases vary somewhat with the composition, reaching a maximum of 11°C. for a mixture containing about 4 per cent of methane. The minimum value for a saturated gas occurs in mixtures with 5.5 to 6.0 per cent of methane. The dry gas has its minimum ignition temperature in mixtures containing 4.5 to 5.0 per cent methane. The results obtained for mixtures where the humidity was 20 per cent seem to coincide with those for the dry gas, but the values for the 50 per cent humid mixtures lie between those of the dry and saturated mixtures, being nearer to the dry gas values. The effect of proportions of water vapor less than 20 per cent were too slight to be decided by these tests. Studies of the influence of water vapor by Bunte and Bloch,[41] on various gas mixtures, revealed that in the case of carbon monoxide the ignition temperature was lowered, presumably because of the presence of hydrogen and hydroxyl radicals participating in the intermediate oxidation steps. Water vapor, however, raised the ignition temperature of hydrogen.

EFFECT OF VARIOUS INERT AND OTHER ADMIXTURES ON IGNITION TEMPERATURES

When argon[42] was added to methane-oxygen mixtures (containing 3 and 37 per cent methane) 3 limits of ignition were found to exist between 635° and 680°C. Although the inert gas did not affect the time lag of ignition, the lower and higher limits at 650°C. were extended, the lower limit change being in accordance with Semenov's law.[48]

[41] K. Bunte and A. Bloch, *Gas u. Wasserfach*, 1935, **78**, 537; *Chem. Abs.*, 1935, **29**, 6731; *Brit. Chem. Abs.* **B**, 1935, 933.

[42] M. B. Neumann and A. I. Serbinov, *Physik. Z. Sowjetunion*, 1933, 4, 423; *Chem. Abs.*, 1934, **28**, 1236.

[48] Semenov's law is a chain-mechanism theory developed to account for both slow reactions and explosions. The probability δ of a collision between activated reaction product and one of the reactants with sufficient energy to start branching of the stoichiometric chain increases with the temperature. If ν is the number of single reactions in the simple chain and n_0 is the specific rate of

The ratios of the concentration of argon to nitrogen and helium necessary to raise the lower limit of a methane-air mixture to one atmosphere were found by Lavrov[44] to be 1.2 and 1.73, respectively. For hydrogen-air mixtures the ratios of the concentrations of carbon dioxide, hydrogen chloride and helium to nitrogen are 1.05, 1.06 and 0.26, respectively.

Tawada[45] found that the addition of 0.1 to 0.2 per cent of ozone lowered the spontaneous ignition temperature of gasoline in an oxygen-nitrogen mixture and at the same time always shortened the lag of ignition. The addition of lubricating oils to various gasolines was found to lower the ignition temperatures. Mineral oils were found to be more effective in this respect than castor oil.[46]

IGNITION TEMPERATURE BY DROP METHOD ON PARTIALLY ENCLOSED PLATE

The apparatus used in these experiments[47] is shown in Fig. 233, the essential features being the ignition block with its cup-shaped surface for holding the material under study, the thermocouple which is inserted in a well below the cup and an aperture centered above the cup for admitting the sample. A tube built into the apparatus permits compressed air to be blown into the cup thus removing all contaminating vapors present before each run. The apparatus is also completely insulated. The investigators observed that on correlating average boiling-point and gravity (A.P.I.) with the values for the ignition temperature of petroleum fractions studied, the temperature falls with increase in the boiling point to about 600°F. in the kerosene range, after which a sudden rise to 800°F. for spontaneous ignition temperature takes place in the lubricating oil range, as shown graphically in Fig. 234. With increased gravity the ignition temperature falls sharply to a minimum and then rises slowly to a maximum. From these data the

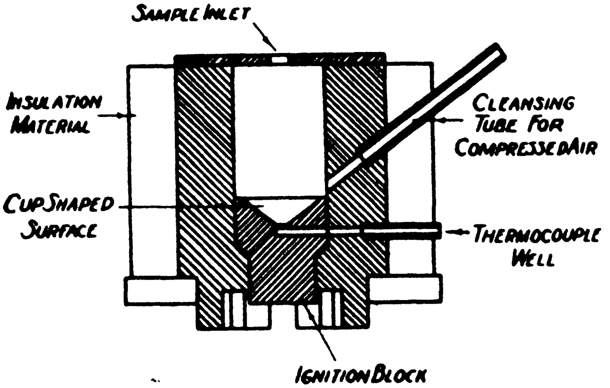


FIG. 233. Cross Section of Closed Chamber for Determination of Spontaneous Ignition Temperatures. (P. J. Wiezevich, J. M. Whiteley and L. B. Turner)

Courtesy Industrial and Engineering Chemistry

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the endothermic reaction, the velocity $= n_0\nu$. When secondary activation is considered, the velocity is $w = n_0\nu(1 - \nu\delta)$. When $\nu\delta = 1$, $w = \propto$ and the reaction is an explosion. The alterations in ν resulting from admixture of an inert gas and from collisions with the vessel walls are discussed. N. Semenov, *Z. physik. Chem.*, 1929, 2B, 161; *Chem. Abs.*, 1929, 23, 2870; *Brit. Chem. Abs.* A, 1929, 514.

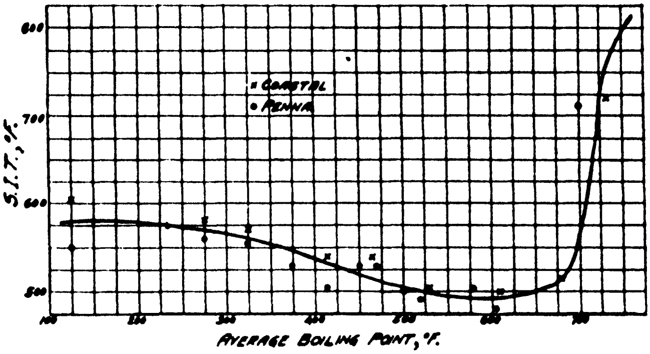
[44] F. A. Lavrov, *Physik. Z. Sowjetunion*, 1933, 4, 787; *Chem. Abs.*, 1934, 28, 2979. See M. J. van der Wal, *Rec. trav. chim.*, 1934, 53, 97; *Brit. Chem. Abs.* A, 1934, 368.

[45] K. Tawada, *J. Soc. Chem. Ind., Japan*, 1935, 38, 270; *Brit. Chem. Abs.* B, 1935, 935; *Chem. Abs.*, 1935, 29, 6748.

[46] T. Araki and S. Otsu, *J. Soc. Chem. Ind., Japan*, 1933, 36, 589; *Chem. Abs.*, 1934, 28, 886; *J. Inst. Pet. Tech.*, 1934, 20, 74A; *Brit. Chem. Abs.* B, 1934, 133.

[47] P. J. Wiezevich, J. M. Whiteley and L. B. Turner, *Ind. Eng. Chem.*, 1935, 27, 152; *Chem. Abs.*, 1935, 29, 2700; *Brit. Chem. Abs.* B, 1935, 889; *J. Inst. Pet. Tech.*, 1935, 21, 123A. See O. Kruber and W. Schade, *Brennstoff-Chem.*, 1934, 15, 404; *Chem. Abs.*, 1935, 29, 1694; *Brit. Chem. Abs.* A, 1935, 41, for the auto-ignition points of a number of hydrocarbons and oxygen compounds.

conclusion was reached that the structure of hydrocarbons may be studied from their spontaneous ignition temperatures. It was also reported that for hydrocarbons having the same number of carbon atoms the spontaneous ignition temperature decreases in the order: aromatic compounds, alkylated aromatic compounds, naphthenes, straight-chain paraffins, branched-chain paraffins and unsaturated aliphatic compounds.



Courtesy Industrial and Engineering Chemistry

FIG. 234.—Comparison of Boiling Points and Spontaneous Ignition Temperatures of Petroleum Fractions. (P. J. Wiezevich, J. M. Whiteley and L. B. Turner)

COMBUSTION OF HYDROCARBONS UNDER CONSTANT VOLUME

Akita[48] reports that reaction temperatures in the oxidation of hydrocarbons vary with concentration of the hydrocarbon, the material used in the construction of the reaction tube, and other conditions. The mechanism proposed for combustion of normal paraffins is:

$$C_nH_{2n+2} \xrightarrow{O} C_nH_{2n+1}OH$$
$$C_nH_{2n+1}OH \xrightarrow{O} C_{n-1}H_{2n} + HCHO$$
$$HCHO \xrightarrow{O} H_2O + CO(\text{or } CO_2)$$

This work was extended to include the alcohols and phenols of the benzene series for which were proposed the following mechanisms.

(1)
$$C_6H_6 \xrightarrow{O} C_6H_5OH$$
$$C_6H_5OH \xrightarrow{O} CO_2 + H_2O$$

(2)
$$C_6H_5CH_3 \xrightarrow{O} C_6H_5CH_2OH$$
$$C_6H_5CH_2OH \xrightarrow{O} C_6H_6 + HCHO$$

(3)
$$C_6H_4(CH_3)_2 \xrightarrow{O} C_6H_4(CH_2OH)_2$$
$$C_6H_4(CH_2OH)_2 \xrightarrow{O} C_6H_6 + 2HCHO$$

(4)
$$C_6H_5(CH_2)_nCH_3 \xrightarrow{O} C_6H_5(CH_2)_nCH_2OH$$
$$C_6H_5(CH_2)_nCH_2OH \xrightarrow{O} C_6H_5(CH_2)_{n-1}CH_3 + HCHO$$
$$HCHO \xrightarrow{O} H_2O + CO + CO_2$$

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[48] Y. Akita, *J. Fuel Soc. Japan*, 1934, 13, 277; *Chem. Abs.*, 1934, 28, 4580; *Brit. Chem. Abs.* B, 1934, 487.

This investigator also noted that the temperature at the beginning of the reaction of the hydrocarbons coincided with the spontaneous ignition temperatures.

INFLUENCE OF CATALYSTS ON IGNITION TEMPERATURES

Zerbe and co-workers[49] studied the ignition temperatures of benzene and pentane vapors in the presence of palladium and the oxides of cobalt, uranium, cadmium, manganese, nickel, magnesium, zinc, tin, lead, chromium, iron, bismuth, vanadium, aluminum and copper. For benzene vapors the ignition temperatures were considerably reduced by the presence of the above solids with the exception of aluminum oxide, lead oxide (yellow) and cuprous oxide. When pentane vapors were substituted for benzene the ignition temperatures were in general raised. In the catalytic combustion of methane-air mixtures, using an electrically heated platinum wire, it was noted by Davies[50] that as the hydrocarbon concentration was increased from 1 per cent to 5 per cent the minimum temperature of combustion was lowered from 970° to 760°C. The mechanisms of the catalytic combustion of carbon monoxide and of hydrogen were found to be different from that of methane. Although it was noted that the entire wire was not catalytically active until heated to 1300°C., in mixtures (of methane and air) where there was an excess of methane the reaction was observed to start below this figure and the temperature of the wire increased abruptly. If the wire temperature was then raised electrically it was noticed that the rate of combustion decreased and became zero at sufficiently high temperature, thus destroying the catalytic effect. When oxygen replaced air, the temperature of incipient combustion rose and the rate of combustion decreased. Davies thus proposed that the catalytic combustion of methane on platinum requires the adsorption of both methane and oxygen.

IGNITION BY COMPRESSION METHODS

The ignition of methane-air mixtures (composition 3-75 per cent methane by volume) by compression methods was investigated by Wheeler.[51] The ignitions were carried out in a pressure cylinder which was in turn connected with a low-pressure chamber by a small aperture. Ignition took place in the pressure cylinder only when the aperture connecting with the low-pressure chamber, containing a similar mixture, was not greater than 2.25 mm. in diameter. Flames shooting into the low-pressure chamber did not ignite its contents. Investigations were carried out in which each hole was covered with a thin copper diaphragm to delay the escape of gas until sufficient pressure had been built up to burst the diaphragm. Under these conditions, (with a hole 4.75 mm. and a diaphragm 0.10 mm. thick, breaking pressure of 110 atmospheres) ignition took place in the low-pressure chamber with mixtures whose concentration varied from 8 to 11 per cent in the pressure cylinder. Wheeler has also reported that the ignition of mixtures by passage of a compression wave which heats them only momentarily was not possible.

Observations have also been made by Dixon and Harwood[52] on the ignition

[49] C. Zerbe, F. Eckert and H. Jentzsch, *Angew. Chem.*, 1933, **46**, 659; *Brit. Chem. Abs.* **A**, 1933, 1253. *Chem. Abs.*, 1934, **28**, 304.

[50] I. W. Davies, *Phil. Mag.*, 1936, **21**, 513; *Chem. Abs.*, 1936, **30**, 3707; *Brit. Chem. Abs.* **A**, 1936, 571. See B. W. Bradford, *J.C.S.*, 1934, 1276; *Chem. Abs.*, 1935, **29**, 11; *Brit. Chem. Abs.* **A**, 1934, 1182 for a discussion of the catalytic action of silver on the combustion of carbon monoxide. Also E. Briner and J. Carceller, *Arch. sci. phys. nat.*, 1935, **17**, 85; *Brit. Chem. Abs* **A**, 1935, 1466. M. J. Oliviéro, French P. 777,917, 1935; *Chem. Abs.*, 1935, **29**, 4552.

[51] R. V. Wheeler, *Trans. Inst. Min. Eng.*, 1935, **88**, 447; *Brit. Chem. Abs.* **B**, 1935, 483; *Chem. Abs.*, 1935, **29**, 3841. *Coll. Guard.*, 1935, **150**, 248; *Brit. Chem. Abs.* **B**, 1935, 1124; *Chem. Abs.*, 1935, **29**, 3161.

[52] H. B. Dixon and J. Harwood, *Safety in Mines Research Board (Gr. Brit.)*, Paper No. 93, 1935; *Chem. Abs.*, 1935, **29**, 7078. See also A. Pignot, *J. Usines Gaz.*, 1932, **56**, 594. *Brit. Chem. Abs.* **A**, 1934, 150.

temperatures of varying concentrations of methane by compression methods. With 7 to 7.5 per cent methane by volume the lowest values were obtained at about 450°C. at 29 atmospheres. Mixtures from 2 to 75 per cent methane could be ignited and were found to propagate flame under higher compression and at the temperature produced by the compression. With increased pressures the ignition temperatures were observed to fall, e.g., at a pressure of one atmosphere the temperature was 735°C. but at 37 atmospheres it fell to 375°C.

IGNITION BY ELECTRICAL DISCHARGE

Experiments[53] on the inflammation of mixtures of air with methane, ethane or carbon monoxide were carried out in a closed spherical vessel in which ignition (from a secondary electrical discharge) took place at the center. This occurred more quickly when the mixture remained quiescent whereas the effect of turbulence was to require a higher ignition current. Explanation was made on the basis that general inflammation of a mixture is dependent on the production of a sufficient volume of flame around the spark-gap. If the heat so generated is dissipated by the rapid delivery of a stream of unburned and unheated mixture (which is the effect of turbulence) the flame is extinguished. Thus, to compensate for such a heat loss, it becomes necessary to use a more intense secondary discharge for ignition.

Gimmelman and Neiman[54] propose that the spark energy of methane-oxygen mixtures increases as the pressure is lowered, according to the empirical formula of Kontorova.[55] It was noted that as a function of the electrode separation, the critical energy is constant for large separations while it increases rapidly for smaller ones. Another factor believed to have influence on the critical energy is the temperature, i.e., the energy value is raised with decreasing temperature, the logarithm of the energy being proportional to the reciprocal of the temperature. These explanations and results were derived theoretically on the assumptions of a chain mechanism for the ignition process and the creation, by the spark, of active centers proportional in number to the energy of the spark.

Yumoto,[56] working with mixtures of air containing less than 5 per cent hydrogen or less than 10 per cent carbon monoxide, found that the igniting power of a short spark (i.e., one less than 4 mm.) which shows band spectra is greater than that of one exhibiting spark spectra. With long sparks (10 to 12 mm.) the igniting power was greatest on the portions of the spark where the heads of the nitrogen band appear strongly, and especially on the negative side of the spark where the heads of the first negative band are superimposed on the enhanced positive band. Yumoto reports that in a carbon monoxide-oxygen mixture (carbon monoxide 7 per cent by volume) if 0.3 per cent nitrogen was present the nitrogen bands were still bright and coincided with the maximum igniting power of the spark. Further investigations showed that the energy of the spark necessary for ignition decreased upon the addition of nitrogen up to 5 per cent (volume) after which slight increases were noted. Other observations, from plotting the amperage against the percentage of nitrogen, revealed a decided discontinuity between the interval 30-35 per cent nitrogen corresponding approximately to the composition of two volumes of oxygen to one of nitrogen. Therefore, Yumoto concluded that nitrogen is not merely a diluent, but that its action may be due to the formation of some compound.

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[53] R. V. Wheeler, *Fuel*, 1935, **14** (5), 147; *J. Inst. Pet. Tech.*, 1935, **21**, 253A; *Brit. Chem. Abs.* B, 1935, 708; *Chem. Abs.*, 1935, **29**, 8333. For data concerning the combustion of methane, ethylene, and acetylene at from 50 to 1800 volts see A. E. Malinovskii and F. A Lavrov, *J. Phys. Chem.* (*U.S.S.R.*), 1931, **2**, 530; *Chem. Abs.*, 1933, **27**, 5515. For investigations carried out to ascertain the relationship between detonation and electrical conductivity in the liquid phase of hydrocarbon fuels see C. Salceanu and D. Gheorghiu, *Bul. soc. romane fiz.*, 1933, **35**, 103; *Chem. Abs.*, 1934, **28**, 3570; *Brit. Chem. Abs.* **A**, 1934, 240.

[54] G. A. Gimmelman and M. B. Neiman, *Compt. rend. acad. sci.* (*U.R.S.S.*), 1934, **4**, 35; *Chem. Abs.*, 1935, **29**, 1985; *Brit. Chem. Abs.* **A**, 1935, 172. It has been found that under otherwise like conditions and with the same voltage and current strengths, the effect of either direct or alternating current on the ignition of methane-air mixtures by electric sparks was the same in principle. For further details see N. I. Brashnik, A. E. Malinovskii and K. A. Skruipnikov, *J. Tech. Phys.* (*U.S.S.R.*), 1934, **4**, 1485; *Chem. Abs.*, 1935, **29**, 8333.

[55] T. A. Kontorova, *J. Phys. Chem.* (*U.S.S.R.*), 1933, **4**, 64; *Chem. Abs.*, 1933, **27**, 3334, finds ignition is due to temperature effect as indicated by equation $\log p/\sqrt{ct^2} = (A/\sqrt{ct^2}) + B$ relating pressure, capacity and voltage.

[56] K. Yumoto, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), 1933, **21**, 246; 1935, **27**, 275; *Brit. Chem. Abs.* **A**, 1933, 1123; 1935, 1327; *Chem. Abs.*, 1933, **27**, 5645; 1935, **29**, 8333.

Investigations carried out by Cohn and Spencer[57] on the effect of density and temperature on the inflammation of a hydrogenated safety fuel brought out some very interesting points. A 5-minute interval was allowed between the fuel injection into the explosion chamber and the spark so that vaporization took place completely. Otherwise for shorter intervals the explosions occurred with liquid-vapor mixtures. For the vapor-air explosions it was noted that an increase in air density lengthened the reaction time. On the other hand, for liquid-vapor-air explosions, an increase in air density from 0.00473 to 0.0095 g./cc. shortened the time of reaction. However, as the density was increased to 0.0142 g./cc., the reaction time again lengthened. The leanest mixture that would explode within a period of 5 minutes was, according to Cohn and Spencer, one corresponding to an air-fuel ratio of 20.7. For a period of 0.004 second it corresponded to one of 25. It was concluded that with an air-fuel ratio of 10 the reaction time was a minimum while the pressure was a maximum for the delayed explosions. At the higher densities and temperatures the two types of explosions acted more alike.

Coal gas-air mixtures have been studied by Sloane[58] who reports that these cannot be ignited by electric discharges between the surfaces of good insulators. Instead, he recommends using a discharge from an insulating surface to a metallic one and also a discharge between two surfaces of moderately good insulators. This type of ignition (by corona discharge) was found to work quite satisfactorily. Induction-coil discharge between glass electrodes at 100°C. produced ignition in a 15 per cent gas-air mixture. As a result of this and further experiments the conclusion was reached that the electrode temperature and the least igniting energy are lower the more concentrated the inflammable mixture. Ignition was possible between slate electrodes (4 mm. apart, with or without metal points) by means of corona discharge provided the discharge current was greater than 300 microamperes.

INCREASE OF PRESSURE DURING COMBUSTION

The question of the effect of initial temperature on the rate of pressure rise in gaseous explosions is a subject still open to investigation. Studies have been made by Pearl and Brown[59] using equipment (shown in Fig. 235 and 236) which consisted essentially of four bombs machined from solid blocks of steel. Bomb 2 of Fig. 235 had two plate-glass windows with a lens in front of each to focus the light emitted by the flame of the burning gas on a rotating drum, thus enabling measurements to be made of the time necessary for the flame to fill the bomb and also of its duration. Bombs 1 and 3 (the former not shown) differed materially in size only. Unlike bomb 2 they had no windows, were heated by gas burners, and cooled by water running over them, and their removable jackets could be filled with solid carbon dioxide. Bomb 4 was small enough to be immersed in a wide-mouthed Thermos bottle containing liquid air. Another part of the equipment was a two-cylinder four-cycle engine, one cylinder of which was operated by a pump, the other as a four-cycle gas engine being connected to a large synchronous motor operating at 1200 r.p.m. The drum shown in Fig. 235 carrying a sensitive bromide paper was held at a constant speed by a synchronous motor.

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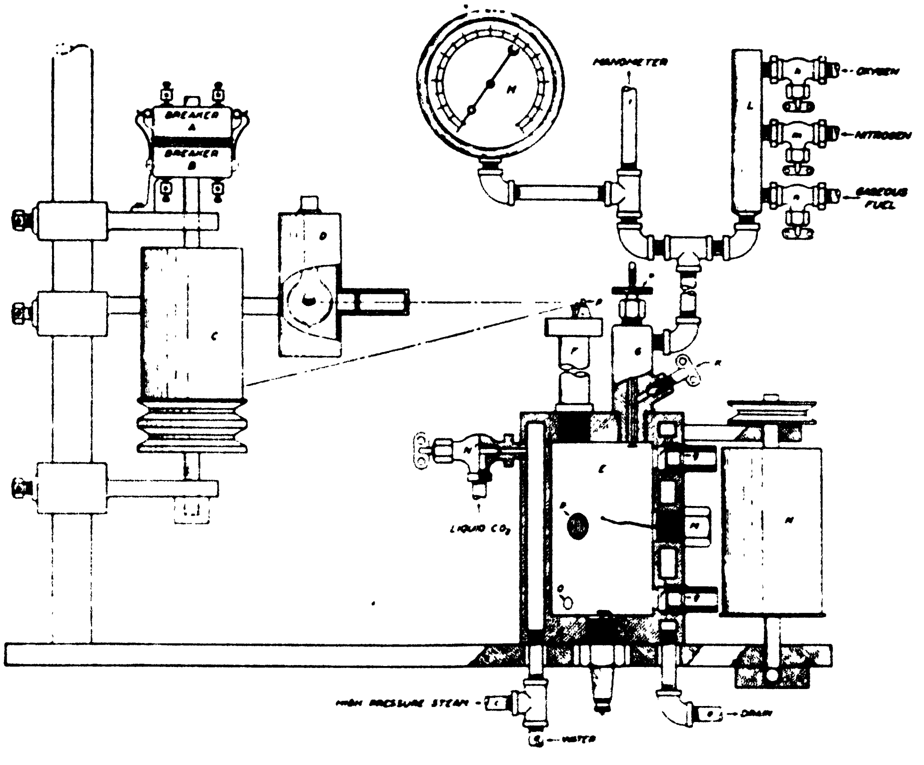
[57] M. Cohn and R. C. Spencer, *Natl. Advisory Comm. Aeronaut. Rept.*, No. 544, **1935**; *Chem. Abs.*, 1936, **30**, 2725.

[58] R. W. Sloane, *Phil. Mag.*, 1935, **19**, 998; *Chem. Abs.*, 1935, **29**, 5753; *Brit. Chem. Abs.* **A**, 1935, 708.

[59] W. A. Pearl and G. G. Brown, *Ind. Eng. Chem.*, 1936, **28**, 1058; *Chem. Abs.*, 1936, **30**, 7345. *Brit. Chem Abs.* **A**, 1936, 1208; *J. Inst. Pet. Tech.*, 1936, **22**, 517A.



Courtesy Industrial and Engineering Chemistry

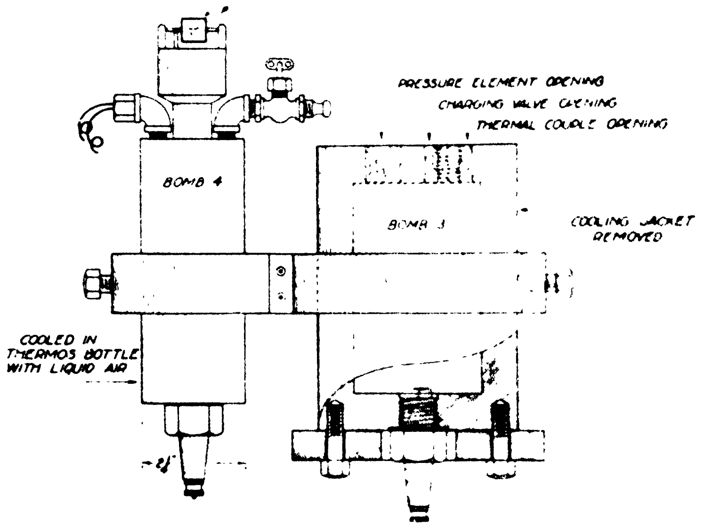
FIG. 235.—Apparatus Assembly for Study of Gaseous Explosions. (W. A. Pearl and G. G. Brown)

C. Rotating drum
D. Light
F. Windows
G. Charging valve
H. Gage
K. Valve

L. Header
M. Opening for thermocouple
N. Rotating drum
P. Opening for spark plug
g. Lens
t. Manometer

In conducting the tests, the bombs were first thoroughly purged by running nitrogen through them at above 100°C. Some of the gases studied were: acetylene, benzene, butane, carbon disulphide, ethylene, hydrogen, methane and propane. The initial weight or density of the charge was kept constant for each series of runs. Pearl and Brown observed a critical initial temperature from which the rate of pressure rise was higher than from other initial temperatures. An excess of oxygen above that theoretically needed for complete combustion, excess fuel or the presence of an inert gas (nitrogen or carbon dioxide) raised this critical initial temperature. When no diluent was present with the mixture theoretically required, the rate of rise in pressure increased uniformly as the initial temperature was lowered and no critical ignition temperature could be reached for such charges. On the other hand, in the presence of 64.7 per cent (volume) nitrogen, 13.9 per cent excess oxygen raised the critical temperature 43°C. This temperature point would have been raised 166°C. had the excess oxygen been replaced by nitrogen.

These investigators also found that when the heat capacities of the products of combustion had low temperature coefficients the explosive mixtures had high critical initial temperatures. The order of decreasing temperature coefficients was: carbon dioxide, carbon monoxide, nitrogen, oxygen, water and hydrogen; so that as the predominating products of the combustion varied from carbon dioxide to hydrogen the critical initial temperature of the explosive mixture rose. For fuels having high carbon to hydrogen ratios, this value was somewhat lower, decreasing as the ratio above increased. Another feature noted was that the critical initial temperature values at constant initial pressures were lower than at constant initial density for theoretical or nearly theoretical mixtures containing little diluent nitrogen. On the other hand, for those mixtures possessing as much or more diluent nitrogen than is in air, the critical initial temperature was higher at constant initial pressure.



Courtesy Industrial and Engineering Chemistry

FIG. 236.—Diagram of Bombs Employed in Study of Gaseous Explosions. (W. A. Pearl and G. G. Brown)

Wellard,[60] after working with fuel-air mixtures comprising ethylene, amylene and ethyl alcohol under pressures of 1, 2, and 4 atmospheres and varying rates of heating, reports with those substances having ignition temperatures above 300°C., an increase in the rate of heating causes an increase in the pressure rise due to the ignition. For example, with a speed of heating of 25° per minute and a mixture containing 38 per cent amylene, the pressure increased with temperature uniformly except when the latter was about 311°C. Wellard proposed that an initial pressure of at least 2 atmospheres and a heating rate of at least 9° per minute seem to be necessary for the spontaneous ignition of amylene-air mixtures. Further observations carried out on gasoline and hexane with ignition temperatures below 300°C. showed a decrease in pressure rise (due to ignition) with increase in the rate of heating, and above a critical rate no longer showed an ignition temperature. Measurements of the pressure rise or "shock" caused by the ignition (spontaneous or by spark), showed that it increased with temperature and was greatest at that of spontaneous ignition.

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[60] R. Wellard, *Ann. combustibles liquides*, 1936, 11, 275; *Chem. Abs.*, 1936, 30, 5015; *Brit. Chem. Abs.* B, 1936, 1029. See *Nat. Pet. News*, 1937, 29 (16), 156.

Investigations were carried out by Mondain-Monval and Wellard[61] on the influence of temperature in the explosion of mixtures of air and hexane vapors. These mixtures were heated in a steel bomb under a pressure of 5 kilograms, and, at a given temperature, fired with a spark. The resultant pressure rise was measured by ascertaining the distance a steel point on the end of a small cylindrical piston was driven into a block of lead. The explosion forces were then plotted against the various firing temperatures. In this manner the graphical data showed that below 180°C. the explosion pressure was independent of temperature, but above this the explosion pressure increased considerably as the spontaneous ignition temperature of 232°C. was approached. This was believed to be the result of formation of alkyl peroxides. When benzene was substituted for hexane quiet combustion took place over the above temperature range, the explosion pressures being independent of firing temperature.

FLAME PROPAGATION

A theory of flame propagation, intended to supply a knowledge of the structure of the flame front during slow inflammation, has been proposed by Lewis and von Elbe.[62] The assumption is made that the highly energized atoms or radicals formed in the flame front play a more important part than heat conductivity in making the unburned gas reactive. It is thought that a small number of these energized atoms diffuse into the unburned phase and initiate chemical reaction. The sum of the thermal and chemical energy per unit of gas in all layers from the burned to the unburned phase is assumed to be constant.

The propagation of flame in fire damp explosions has been studied by Burgess[63] who reported that from observations of the explosion of methane-air mixtures in tubes having branch members at right-angles to the main tube the total distance of projection of the flame depends on the amount of release afforded to the pressure of the explosion. He assumed that by the addition of one or more side tubes ahead of the flame it is possible to increase its distance of projection. On the other hand, if a side tube joined the main tube in the region of the explosive mixture, instead of just beyond it, the distance of projection was less. The maximum total distance of projection reported by Burgess was approximately 7.25 times the original length of the explosive mixture.

[61] P. Mondain-Monval and R. Wellard, *Ann. combustibles liquides*, 1935, **10**, 278; *J. Inst. Pet. Tech.*, 1935, **21**, 253A; *Bull. soc. encour. ind. natl.*, 1935, **134**, 582; *Chem. Abs.*, 1936, **30**, 2737; *Compt. rend.*, 1935, **200**, 232; *Chem. Abs.*, 1935, **29**, 1973; *Brit. Chem. Abs.* **A**, 1935, 307.

[62] B. Lewis and G. von Elbe, *J. Chem. Physics*, 1934, **2**, 537; *Brit. Chem. Abs.* **A**, 1934, 1179; *Chem. Abs.*, 1934, **28**, 7015. For a discussion of the problems of ignition and flame propagation see W. Jost, *Z. Electrochem.*, 1936, **42**, 461; *Chem. Abs.*, 1936, **30**, 6919.

[63] M. J. Burgess, *Safety in Mines Research Board*, Paper No. 83, 1934; *Brit. Chem. Abs.* **B**, 1934, 707; *Chem. Abs.*, 1934, **28**, 7018. See also H. F. Coward and R. V. Wheeler, *Safety in Mines Research Board*, Paper No. 82, 1934; *Brit. Chem. Abs.* **B**, 1934, 307.

Flame observations in an engine have been reported by Marvin.[64] A side-valve L-head single-cylinder engine was employed, equipped with a special head containing 30 windows and apparatus consisting of mirrors, lenses and a stroboscope fitted with a phase-changing device, enabling one to look down vertically through each window without altering the eye position. Thus it was possible alternatively to substitute a camera at the eye piece and take photographs of the various settings using the stroboscope as a high-speed shutter for the camera with each series of exposures taking 30 seconds. Progress of the flame front at any degree of crank angle was observed from the position of the windows illuminated. The photographs showed that the flame progresses in patterns roughly concentric about the point or points of ignition. "Reaction velocity" was defined as the rate at which the flame front progresses into the unburned gases. The "gas velocity" merely expresses gas motion and involves no burning. Reaction velocity has been found to vary greatly with different fuels, approaching a maximum near the equivalent mixture for any given fuel. This value may be reduced by the addition of inert gases. Marvin proposes that the flame velocities are a maximum at roughly the middle of inflammation relative to crank angle and at a minimum at the beginning and end.

STATIONARY FLAME AND ITS UTILIZATION

It has been found by Kurokawa[65] that to maintain a steady flame at the orifice of a burner the ignitible gas and air (mingled by diffusion) must flow upward at a rate just balancing that at which the flame is propagated downward. If it is assumed that combustion takes place at the conical boundary surface between the flame and a mixture containing the theoretical amount of air for complete combustion, and that neither thermal decomposition, nor partial ignition, occurs in the flame, the following relationship then exists, where v is the velocity of ignition

$$v = \frac{(1 + \alpha)Q}{\pi r\sqrt{L^2 + \gamma^2}}$$

under the theoretical air mixture, Q the quantity of gas issuing from the orifice, α the theoretical air volume of gas, L the length of the flame, and γ the radius of the orifice. When the supply pressure of gas is h, the specific gravity s, and the orifice constant K, we have the expression for Q given below.

$$Q = K\pi r^2\sqrt{h/s}$$

Therefore,

$$L = (1 + \alpha)\gamma\sqrt{h/v}\sqrt{s}$$

when γ is much less than L. This relationship Kurokawa found to hold experimentally within certain limits. Velocity of propagation of flame has also been determined by Corsinglia[66] and found inversely proportional to the square root of the specific gravity. Moreover, since the velocity v may be considered as that of the gas and air mixture produced by diffusion and gas flow from an orifice, the same relation may be derived from kinetic theory. For this reason Kurokawa reports the product $v\sqrt{s}$ is constant. The relationship was thus expressed in a straight-line equation, $H = A + BL$, in which A and B are constants. From the experimental work in which A and B were determined, it was noted that gases rich in hydrocarbons give comparatively satisfactory results, although gases containing a large proportion of inert diluent or hydrogen do not.

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[64] C. F. Marvin, Jr., *J. Soc. Automotive Eng.*, 1934, **35**, 391; *J. Inst. Pet. Tech.*, 1935, **21**, 29A; *Chem. Abs.*, 1935, **29**, 910. See also K. Schnauffer, *J. Soc. Automotive Eng.*, 1934, **34**, 17. E. M. Dodds and C. H. Sprake, *Engineering*, 1935, **149**, 183; *J. Inst. Pet. Tech.*, 1935, **21**, 403A. M. Precoul, *Rev. pétrolifère*, 1936, **688**, 905; *Chem. Abs.*, 1936, **30**, 7317. J. Breton, *Ann. combustibles liquides*, 1936, **11**, 487; *Brit. Chem. Abs.* **A**, 1936, 1343; *Chem. Abs.*, 1936, **30**, 5565.

[65] M. Kurokawa, *J. Fuel Soc., Japan*, 1933, **12**, 1346; *Chem. Abs.*, 1934, **28**, 1236; *Brit. Chem. Abs.* **B**, 1934, 179. For the measurement of radiation and the mechanism of reaction in flames see V. E. Garner, *J. Phys. Chem. (U.S.S.R.)*, 1931, **2**, 509; *Chem. Abs.*, 1933, **27**, 5514.

[66] J. Corsinglia, *Am. Gas. Assoc. Monthly*, 1931, **13**, 437; *Chem. Abs.*, 1932, **26**, 1752.

Investigations have also been carried out by Malinovskii and Klass[67] on the effect of temperature on the interruption of gas explosion by an electric field. These collaborators found that the minimum potential required to extinguish a nearly stationary flame between condenser plates was lower at all temperatures for a mixture consisting of 25 and 75 per cent of acetylene and air, respectively, than for a similar mixture where proportions were 20-80 per cent. Although the temperature coefficient was positive in both cases it was reported to be greater for the 20-80 per cent mixture, the flame of which was not quenched by any potential up to 1500 volts at temperatures greater than 120°C.

TEMPERATURE AND LATENT ENERGY IN FLAME GASES

The general assumption that temperatures reached as a result of the combustion of gases are equal to those calculated from the heat of combustion of the fuel and the specific heats of the products of combustion, making allowance for heat lost by radiation is reported to be in error.[68] From temperature measurements made by means of platinum thermometry during the long period of constant pressure burning (the "pre-pressure period"), it was found that the flame gases are in an abnormal condition and do not consist of merely heated carbon dioxide, steam, nitrogen or other gases. When this abnormal condition prevails, associated with it is a latent energy of large amount, and it is this factor which prevents the full development of the calculated temperatures in the inflamed gases, according to David. At atmospheric pressure the latent energy is reported to be seldom less than 15 per cent of combustion.

Another series of experiments was carried out in which the light emitted by inflamed gases contained in a closed vessel was recorded on a moving photographic film. A simultaneous pressure record was made and from this the mean temperature of the inflamed gases could be deduced. Marvin found that light was emitted not only during the explosion period, but for some time afterwards. This duration of "after-glow" increased with the density. He therefore concluded that gases, after inflammation, are in an abnormal condition and associated with this condition is latent energy, accounting for the accompanying luminosity.

MEASUREMENT OF FLAME TEMPERATURES BY THE SPECTRAL LINE-REVERSAL SYSTEM

It has been reported by Watts and Lloyd-Evans[69] that such studies have been made in the following manner. Two quartz windows were fitted into the combustion chamber of an engine. Then light from an electric arc was passed through suitable lenses and a pair of adjustable neutral wedges so as to vary its intensity. This light then emerged as a parallel beam which passed through the engine cylinder and emerged through a further lens which focused the beam onto the slit of a spectroscope. Between this latter lens and the spectroscope was inserted a stroboscope disc running at half-engine speed. In this way the light passed to the slit of the spectroscope once in each working cycle of the engine. The wedges previously mentioned were adjusted so that reversal of the sodium line (obtained by introducing a metallic salt in the fuel, e.g., a 1 per cent solution of sodium ethylate in alcohol which was added in the proportion of 15 cc. per gallon) occurred while the engine was running. The engine was then stopped and the spectroscope replaced by a monochromatic pyrometer of the disappearing filament type. Readings were obtained on the pyrometer by removing the quartz window and focusing the lens nearest the spectroscope when engine conditions became steady. In this manner it was found possible to observe temperatures over 1200°C. which could be repeated to within 15°C.

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[67] A. E. Malinovskii and I. A. Klass, *Ber. Ukrain. wiss. Forsch.-Inst. physik. Chem.*, 1934, **3**, 107; *Chem. Abs.*, 1935, **29**, 2743; *Brit. Chem. Abs.*, **B**, 1935, 979. For a study of the electrical conductivity of the flame in an internal combustion engine see D. Abugov and A. Sokolik, *J. Exptl. Theoret. Phys (U.S.S.R.)*, 1933, **3**, 438; *Chem. Abs.*, 1934, **28**, 5630.

[68] W. T. David, *Engineer*, 1934, **157**, 558; *J. Inst. Pet Tech.*, 1934, **20**, 405A; *Chem. Abs.*, 1934, **28**, 6602; *Phil. Mag.*, 1936 (7), **21**, 280; *Brit. Chem. Abs.* **A**, 1936, 432. *Proc. S. Wales Inst. Eng.*, 1936, **51**, 375; *Chem. Abs.*, 1936, **30**, 6617; *Brit. Chem. Abs* **B**, 1936, 258. For a study of flame temperatures in gasoline engines see *Engineering*, 1934, **137**, 623; *J. Inst. Pet. Tech.*, 1934, **20**, 446A. See also W. T. David and A. S. Leah, *Phil. Mag.*, 1936 (7), **22**, 513; *Brit. Chem. Abs.* **A**, 1936, 1343.

[69] S. S. Watts and B. J. Lloyd-Evans, *Proc Physical Soc.*, 1934, **46**, 444; *Brit. Chem. Abs.* **B**, 1934, 564; *Engineering*, 1934, **137**, 362; *J. Inst Pet. Tech.*, 1934, **20**, 303A; *Engineering*, 1935, **139**, 48; *Chem. Abs.*, 1935, **29**, 2720. For a discussion of studies made of the flame temperatures in methane-air mixtures see W. T. David and J. Jordan, *Phil. Mag.*, 1934, **18**, 228; *Chem. Abs.*, 1934, **28**, 7133; *Brit. Chem. Abs.* **A**, 1934, 1073.

Another method for measuring engine flame temperatures has been suggested by Rassweiler and Withrow.[70] The conditions differed slightly from those previously discussed. Temperatures were measured, not at one point in the combustion chamber, but at three; near the point of ignition, near the center of the combustion space, and in the portion of the chamber where the last of the charge was burned and knocking took place if at all. These flame temperature measurements were taken under both non-knocking and knocking conditions instead of as heretofore under only non-knocking. The method of measuring the temperature was the sodium-line reversal. The L-head engine combustion chamber had two windows, placed opposite each other so that light could pass directly from an outside light source through the combustion chamber and the flames and be focused on the slit of a spectroscope. The source of light used was a General Electric projection lamp with a wide strap filament. The temperature was controlled by varying the current through the lamp. Thus from a calibration curve the temperature corresponding to current could be read. A stroboscopic shutter enabled observations in the combustion chamber to be limited to any desired portion of the engine cycle. The essential operating conditions for the engine were: jacket temperature held at 212°F., engine speed 800 r.p.m., spark advance 15°, fuel-air ratio 12 to 1, and compression ratio 4.4 to 1. The fuels used consisted of a 32 octane number gasoline for the knocking runs and a 75 octane number for the non-detonating tests. Powdered sodium carbonate was introduced in the engine to obtain a bright yellow sodium emission line as contrasted with a background of the continuous tungsten filament spectrum. As the temperature of the filament was raised it was noted that the intensity of the sodium emission decreased. When the line disappeared, the temperature of the flame and filament were the same, thus giving the flame temperature from the current-temperature curve.

It was found that under non-knocking conditions, after inflammation was complete, at about 35° past top dead center, a temperature gradient existed in the chamber from the firing end to the locality of final inflammation. For a condition where the engine was knocking, 5° before top dead center, a temperature of 4400°F. absolute at the firing end was recorded. At later angles it increased and rose to a maximum of 5000°F. absolute as the pressure increased. At 15° past top dead center, the temperature rose sharply but fell off rapidly as the pressure decreased. The temperature for the center of the chamber rose suddenly with the pressure until about 15° past top dead center. Temperature measurements could not be made at the knocking end until the knock was completed, at which point the temperature was already dropping. Under knocking conditions the temperatures at the firing end and the center did not appear to equalize, but those of the center and the knocking end approached each other quite closely for 20° after the knock. The temperatures reached a maximum several degrees earlier when the engine was knocking than when it was not. At all three positions the maxima were higher in knocking than in smooth running. During most of the expansion stroke the rate of cooling was faster after knocking than when no knocking had taken place. Heat loss to the walls was concluded to be greater, possibly because of more black-body radiation and because of the turbulence of the gases in knocking.

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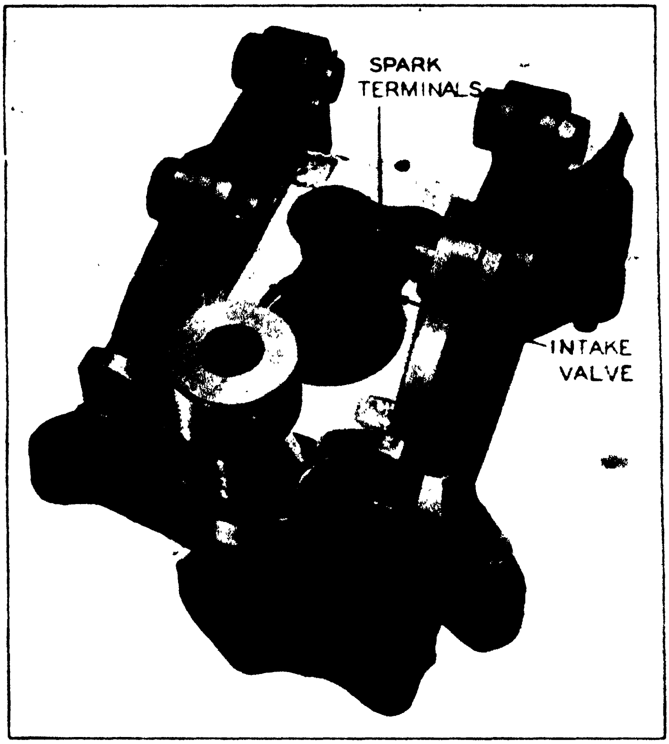
[70] G. M. Rassweiler and L. Withrow, *J. Soc. Automotive Eng.*, 1935, **36**, 125; *J. Inst. Pet. Tech.*, 1935, **21**, 200A; *Chem. Abs.*, 1935, **29**, 3808; *Automotive Ind.*, 1935, **72**, 86; *Chem. Abs.*, 1935, **29**, 1973.



Courtesy General Motors Corp.
Courtesy Industrial and Engineering Chemistry

Fig. 237.—Quartz-Covered Combustion Chamber for Photography of Engine Flames. (G. M. Rassweiler and L. Withrow.)

Flame Velocities in Mixtures of Inflammable Gases

For pentane-oxygen mixtures ignited by an electric spark, Gusev and Neiman[71] report that for a given initial pressure and temperature the mean velocity was proportional to the composition.[72] Using the mixture mentioned above under 7 atmospheres pressure and 175°C. results showed two maxima in the speed of propagation.

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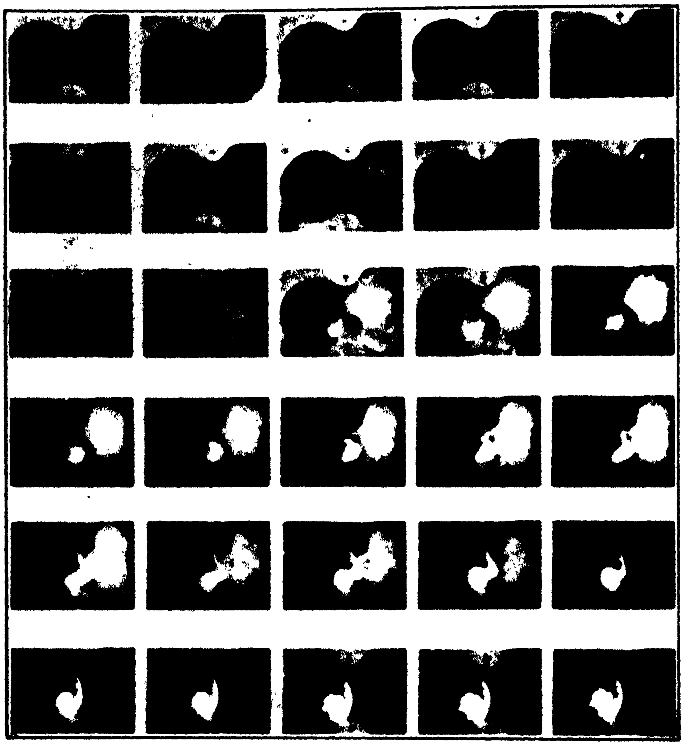
[71] N. N. Gusev and M. B. Neiman, *Compt. rend. acad. sci. (U.R.S.S.)*, 1935, **2**, 377; *Brit. Chem. Abs.* **A**, 1935, 1081; *Chem. Abs.*, 1935, **29**, 6759.

The effect of moist gases on flame speeds was studied by Voronkov and Sokolik[73] who used moist carbon monoxide-oxygen mixtures containing 20-92.5 per cent carbon monoxide. The experiments were carried out with pressures ranging from 200 to 400 mm. At 400 mm. there were sharp maxima for compositions corresponding to $2CO + O_2$ and $4CO + O_2$, and a sharp minimum for the gas mixture represented by $3CO + O_2$. On the other hand, at 200 mm. only the sharp maximum was noted when the ratio of gases was that indicated by $4CO + O_2$. In the explosion of equimolecular mixtures of ethylene and oxygen both undried and intensively dried with phosphorus pentoxide, the flame speeds are reported to be faster in the dried gases.[74]



Courtesy General Motors Corp.

FIG. 238.—Flame Pictures of a Single Engine Explosion. (G. M. Rassweiler and L. Withrow)

Further investigations of the velocity of flame motion have been made by Rassweiler and Withrow,[75] who employed a specially designed single-cylinder L-head engine possessing as its important feature the combustion chamber shown in Fig. 237, and a special motion picture camera constructed so as to be able to use continuous film. Image motion was synchronized by means of 30 lenses carried in a disk mounted on the engine crankshaft and pictures were obtained which presented an unobstructed view of the entire combustion chamber. This camera photographed 30 pictures of a single explosion at rates up to five thousand pictures per second. The pressure-time curve of this explosion was also recorded and is presented in Fig. 239. These flame pictures (Fig. 238) show the ignition spark, the spread of flame through the combustion chamber, gas movements behind the flame front, and an increase in luminosity of the burned gases near the spark plug as the explosion process proceeds and the pressure rises.

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[72] See also F. Schuster, *Gas u. Wasserfach*, 1934, 77, 805; *Brit. Chem. Abs.* **B**, 1935, 53; *Chem. Abs.*, 1935, **29**, 1967.

[73] V. Voronkov and A. Sokolik, *Nature*, 1936, 137, 533; *Chem. Abs.*, 1936, **30**, 3704.

[74] W. A. Bone and J. Bell, *Proc. Roy. Soc. (London)*, 1934, **A144**, 257; *Chem. Abs.*, 1934, **28**, 4580; *Brit. Chem. Abs.* **A**, 1934, 603. For a method of measuring the speed of explosion waves and thereby determining the detonation limits of various gas mixtures, see J. Breton, *Ann. combustibles liquides*, 1936, 11, 487; *Chem. Abs.*, 1936, **30**, 6565; *J. Inst. Pet. Tech.*, 1936, **22**, 468A.

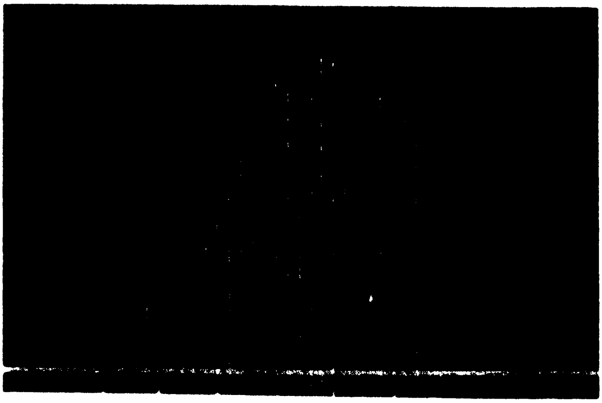

FIG. 239. Pressure Record of Explosion Photographed in Fig. 238. (G. M. Rassweiler and L. Withrow)

Courtesy Industrial and Engineering Chemistry
Courtesy General Motors Corp.

Explosive Behavior of Knocking and Non-knocking Fuels. Investigations of this nature were carried out by Thompson and Wheeler[76] who made photographic records of the flame movements and pressure development of various hydrocarbon-air mixtures. For pentane-air mixtures knock occurred only when pentane was in excess, so that it was supposed the source of the energy of the shock wave responsible for this phenomenon resides in partly burning gases behind the flame front. They noted that a measure of the anti-knock value of a fuel could be obtained either from the lowest initial pressure with which a mixture containing nearly the theoretical quantity of fuel for complete combustion can produce a knocking explosion, or, alternatively, with a constant initial pressure, from the concentration of a fuel required to produce an explosion the flame of which is striated. Thompson and Wheeler further compared the explosive characteristics of pentane, *n*-hexane, benzene, cyclohexane, *n*-heptane, and ethyl alcohol with those of commercial fuels.

These investigators also report that the character of a knocking explosion is completely changed if nitrogen of the air is replaced by either argon or helium, all other conditions remaining the same. For example, a 3.7 per cent pentane-air mixture of an initial pressure of 3 atmospheres and 70°C., gave a strong knock on exploding. On the other hand, detonation of a 3.7 per cent pentane-oxygen-argon mixture under the same conditions of temperature and pressure gave a quiet explosion despite the fact that flame speed in the former mixture was twice that in the latter. Continuous illumination occurred behind the flame front in the pentane-oxygen-argon mixture with regular pressure development. Thus it was concluded that during the later stages of flame propagation in a knockless pentane-oxygen-argon explosion there must be less residual energy than in the knocking pentane-oxygen-nitrogen explosion. It was supposed that nitrogen plays an active part in a knocking explosion, perhaps as an absorber of energy or a producer of oxides.

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[75] G. M. Rassweiler and L. Withrow, *Ind. Eng. Chem.*, 1936, **28**, 672; *Brit. Chem. Abs.* **B**, 1936, 775; *Chem. Abs.*, 1936, **30**, 5774; *J. Inst. Pet. Tech.*, 1936, **22**, 369A. See also G. M. Rassweiler and L. Withrow, *Automotive Eng.*, 1934, **24**, 281, 385; *J. Inst. Pet. Tech.*, 1934, **20**, 524A, 607A. For an analysis of the phenomena of "rough running" in gasoline engines see C. C. Minter, *J. Soc. Automotive Eng.*, 1935, **36**, 89; *J. Inst. Pet. Tech.*, 1935, **21**, 201A; *Chem. Abs.*, 1935, **29**, 3133.

[76] J. K. Thompson and R. V. Wheeler, *J. Inst. Pet. Tech.*, 1935, **21**, 931; *Brit. Chem. Abs.* **B**, 1936, 133; *Chem. Abs.*, 1936, **30**, 3212; *J. Inst. Pet. Tech.*, 1936, **22**, 30A.

MECHANISM OF COMBUSTION

Many investigations have been undertaken on the combustion mechanism as it takes place in the internal combustion engine, principally to determine the cause of knock or detonation. By photographic means, Withrow and Boyd[77] made simultaneous flame and pressure studies of individual explosions in a gasoline engine. The essential feature in the apparatus employed was a special cylinder head fitted with a quartz window so that a camera could be mounted above the window to record pictures of the flames inside the cylinder. Flame and pressure records were synchronized by electrical means. From the records so obtained the following conclusions were made: starting at the point of a spark, a flame, or a narrow combustion zone, moves progressively through the charge. Oxidation is apparently complete within this narrow zone but the products of combustion to the rear of the flame front continue to emit light for a time. In a non-knocking explosion the flame moves at a relatively constant velocity to the end of the combustion space. However, in a knocking explosion the rate of inflammation of the latter portion of the charge is very much higher than normal, so high in fact, that at the instant of knock the flame appears simultaneously throughout the unburned portion of the charge.[78] This phenomenon is accompanied by a very rapid rise in cylinder pressure, the magnitude of which is related to the intensity of the knock.

Subsequent spectroscopic studies[79] revealed that most of the light visible in the afterglow, i.e., points through which the flame front had already passed, came from the same molecular carriers as the light given off during the reaction between carbon monoxide and oxygen. This indicated that the hydrocarbons are burned in the flame front, furnishing confirmatory evidence for the conclusion that in a knocking explosion the sudden pressure rise is due to rapid burning of the last portion of the fuel charge with little or no contribution from the gases through which the flame has already passed. The visible light from the flame front under non-knocking conditions, and also under knocking conditions prior to knock, was

[77] L. Withrow and T. A. Boyd, *Ind. Eng. Chem.*, 1931, **23**, 539; *Chem. Abs.*, 1931, **25**, 3475; *Brit. Chem. Abs.* B, 1931, 618. A previous method of investigation, using a quick-acting water-cooled sampling valve attached to the cylinder for removing gases at any desired time for inspection, proved to be inadequate for differentiating some of the characteristics of knocking and non-knocking explosions. See W. G. Lovell, J. D. Coleman and T. A. Boyd, *Ind. Eng. Chem.*, 1927, **19**, 373; L. Withrow, W. G. Lovell and T. A. Boyd, *ibid.*, 1930, **22**, 945; *Chem. Abs.*, 1927, **21**, 1698; 1930, **24**, 5144; *Brit. Chem. Abs.* B, 1927, 322; 1931, 376. See also M. Brutzkus, *Compt. rend.*, 1934, **199**, 833; *Ann. comb. liquides*, 1935, **10**, 141; *Chem. Abs.*, 1935, **29**, 317; *Brit. Chem. Abs.* B, 1935, 133; 1936, 728. Carleton Ellis, "The Chemistry of Petroleum Derivatives, The Chemical Catalog Co., New York, 1934.

[78] See also, K. Schnauffer, *Z. Ver. deut. Ing.*, 1931 **75**, 455; *Chem. Abs.*, 1931, **25**, 3155; *D. V. L. Jahrbuch*, 1931, 375; *J. Inst. Pet. Tech.*, 1931, **17**, 525A. M. Prettre, *14me Congr. chim. ind. Paris*, 1934; *Chem. Abs.*, 1935, **29**, 6396.

[79] L. Withrow and G. M. Rassweiler, *Ind. Eng. Chem.*, 1931, **23**, 769; *Chem. Abs.*, 1931, **25**, 4383; *Brit. Chem. Abs.* B, 1931, 829. See also, *S.A.E. Journal*, 1936, **39**, 297; *Chem. Abs.*, 1936, **30**, 7317.

found to come largely from CH and C_2 radicals, but when knock began, absorption bands from those radicals appeared only feebly in the flame front. Since OH radicals were also detected in the explosion mixtures[80] one suggested explanation for the decreased intensity of CH and C_2 bands was that reactions may have been taking place with these OH radicals in a knocking explosion.

$$\begin{aligned} C_2 + OH &\longrightarrow CO + CH \\ CH + OH &\longrightarrow CO + H_2 \end{aligned}$$

It was advanced that the presence of OH radicals may be the result of the thermal dissociation of water.

Further work[81] indicated that chemical changes occur in the air-fuel mixtures ahead of the flame fronts and that these changes are different in knocking than in non-knocking explosions. The conclusion was made that the observed weakening of the CH and C_2 bands in the knocking zone is the result of the disappearance of a large portion of the original hydrocarbons before arrival of the flames, with the formation of compounds which do not give CH and C_2 radicals when they inflame. Reactions in the knocking zone just prior to inflammation were assumed to be, in part at least, oxidation processes.[82] A reason for the assumption was the detection of formaldehyde as a reaction product in this zone under knocking conditions and its absence from zones ahead of the flame front in non-knocking explosions.[83] Since formaldehyde did not produce knock when introduced into the engine with the intake air, it appeared that the compound is not alone responsible for knock. However, the general relationship between the appearance of this aldehyde and the subsequent occurrence of knock indicated that the compound is associated with a reaction sequence which leads to spontaneous ignition in the non-inflamed gases ahead of the flame front, which ignition was assumed to be the cause of knock.

By varying engine conditions so that the knock intensity was increased from zero upwards, formaldehyde appeared under conditions just below the threshold of knock and increased in concentration to a slight extent after passing conditions of incipient knock, but the concentration soon reached a maximum which was barely altered by more severe knocking. With variables adjusted slightly below the threshold, preflame reactions appeared to take place also, but their progress was so slow that spontaneous inflammation did not occur before the flames reached the end of the combustion chamber.

It was shown that the addition of tetraethyl lead eliminated knocking by retarding the burning of the last part of the fuel charge to a rate which is normal for non-knocking explosions. At the same time the concentration of formaldehyde in the knocking zone was not reduced. However, the use of tetraethyl lead in the fuel to remove knock did restore the intensities of the CH and C_2 bands as detected spectroscopically in the burning gases in the knocking zone. Both atomic lead and lead monoxide were found in the flame fronts and there was strong evidence to assume that the lead monoxide was being reduced in the non-inflamed portion of the fuel charge. Thus, it appeared that this monoxide was acting as an oxidizing agent at the same time that the metallic lead was effecting anti-knock action.[84]

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[80] G. M. Rassweiler and L. Withrow, *Ind. Eng. Chem.*, 1932, **24**, 528; *Chem. Abs.*, 1932, **26**, 3656; *Brit. Chem. Abs.* B, 1932, 585.

[81] L. Withrow and G. M. Rassweiler, *Ind. Eng. Chem.*, 1933, **25**, 923; *Chem. Abs.*, 1933, **27**, 4659; *Brit. Chem. Abs.* B, 1933, 994.

[82] G. M. Rassweiler and L. Withrow, *Ind. Eng. Chem.*, 1933, **25**, 1359; L. Withrow and G. M. Rassweiler, *ibid.*, 1934, **26**, 1256; *Chem. Abs.* 1934, **28**, 886; 1935, **29**, 1235; *Brit. Chem. Abs.* B, 1934, 133; 1935, 581; *J. Inst. Pet. Tech.*, 1935, **21**, 46A.

[83] See also A. Egerton and L. M. Pidgeon, *Proc. Roy. Soc.*, 1933, A142, 26; *Chem. Abs.*, 1934, **28**, 44; *Brit. Chem. Abs.* A, 1933, 1227.

[84] L. Withrow and G. M. Rassweiler, *Ind. Eng. Chem.*, 1935, **27**, 872; *Chem. Abs.*, 1935, **29**, 6748; *Brit. Chem. Abs.* B, 1935, 888; *J. Inst. Pet. Tech.*, 1935, **21**, 404A.

Several workers have assumed that detonation in an engine is a direct result of peroxide formation during combustion. For example, Dumanois[85] noted that, in the direct oxidation of saturated hydrocarbons by air, alkyl peroxides are formed between 200° and 300°C. Also, in operating an engine at 270°C. on a hexane-air mixture under detonating conditions, peroxides and aldehydes were found in the exhaust gases after the ignition had been cut off and the engine kept running with an auxiliary motor. Slight explosions heard after switching off the engine were assumed to be the result of exothermic spontaneous decomposition of peroxides formed during compression. Since it was observed that peroxides begin to form at about 120-130°C. and are decomposed below 300°C., the proposal was made that detonation could be eliminated by operating the engine with a sufficiently high fuel-mixing temperature and great enough speed to pass over the peroxide-forming stage.[86]

In experiments conducted by Serruys,[87] detonation occurred in a one-cylinder engine when the air was preheated to 250°C. With a temperature of 310°C. a severe knock resulted. In view of the fact that peroxides decompose below 300°C., it was concluded that they were not the sole cause of detonation but when present favored its occurrence. The suggestion was made that during combustion the temperature and pressure of the unburned gases increase irregularly so that at some point the inflammation limit is reached prematurely, causing a sudden increase in heat evolution and pressure, which, if sufficiently large, will start an explosive wave which results in knocking.[88] Dumanois[89] assumed that, in knocking explosions occurring above temperatures at which peroxides do not form, the detonation is the result of spontaneous ignition of the charge.[90]

In a critical review of various theories of detonation, Darche[91] gave the following opinions: Detonation results neither from simultaneous combustion of the unburned gases in the latter portion of the charge nor from the propagation of an explosive wave. Although peroxides can produce an accelerating effect at the beginning of combustion they probably no longer exist when detonation takes place and are therefore not the determining cause of this phenomenon. The action of antiknock compounds in small amounts is to retard combustion rather than to act on peroxides. Detonation in engines is characterized by a very rapid, but not explosive, combustion of fresh gases with a concurrent acceleration of combustion of the carbon monoxide existing just behind the flame front so that the phenomenon of knocking is not localized but involves a general acceleration of combustion. Darche considered that an important factor in eliminating detonation is to alter the design of the motor so that an automatic regulation of combustion can be effected to vary with operating conditions.

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[85] P. Dumanois, *Compt. rend.*, 1933, **197**, 393; *Chem. Abs.*, 1933, **27**, 5955; *Brit. Chem. Abs.* **B**, 1933, 850. P. Dumanois, P. Mondain-Monval and B. Quanquin, *Ann. combust. liquides*, 1931, **6**, 559; *J. Inst. Pet. Tech.*, 1931, **17**, 524A; *Compt. rend.*, 1931, **192**, 1158; *Chem. Abs.*, 1931, **25**, 4391.

[86] P. Dumanois, *Ann. combust. liquides*, 1934, **9**, 143; *J. Inst. Pet. Tech.*, 1934, **20**, 300A. See also R. Wellard, *Ann. combust. liquides*, 1936, **11**, 275; *J. Inst. Pet. Tech.*, 1936, **22**, 394A; *Brit. Chem. Abs.* **B**, 1936, 1029; *Chem. Abs.*, 1936, **30**, 5015.

[87] M. Serruys, *Compt. rend.*, 1933, **197**, 1592; 1934, **199**, 1574; **199**, 830, 1184; *Chem. Abs.*, 1934, **28**, 2171; 1935, **29**, 327, 915; *Brit. Chem. Abs.* **B**, 1934, 438; 1935, 133. *Ann. combust. liquides*, 1934, **9**, 331; 1935, **10**, 142; *Chem. Abs.*, 1934, **28**, 6291; *J. Inst. Pet. Tech.*, 1934, **20**, 446A; 1935, **21**, 201A.

[88] For an explanation of detonation in the Diesel engine, see M. Serruys, *Compt. rend.*, 1935, **200**, 1376; *Chem. Abs.*, 1935, **29**, 4564.

[89] P. Dumanois, *Compt. rend.*, 1934, **198**, 30; *Ann. combust. liquides*, 1934, **9**, 333; *Chem. Abs.*, 1934, **28**, 2171; *Brit. Chem. Abs.* **B**, 1934, 438; *J. Inst. Pet. Tech.*, 1934, **20**, 446A. See also C. Dufraisse and R. Chaux, *Compt. rend.*, 1933, **197**, 672; *Chem. Abs.*, 1934, **28**, 302.

[90] Carbonaceous deposits in engine cylinders may have a beneficial influence on detonation as a result of the high temperatures maintained on their surfaces because of poor thermal conductivity. See G. Roberti, *Gazz. chim. ital.*, 1933, **63**, 872; *Chem. Abs.*, 1934, **28**, 5646; *Brit. Chem. Abs.* **B**, 1934, 309.

[91] A. Darche, *Mem. compt. rend. soc. ing. civils France*, 1933, **86**, 969; *Chem. Abs.*, 1934, **28**, 3558; *Brit. Chem. Abs.* **B**, 1934, 354.

Studies of the combustion process in an engine by means of a sampling valve employed to remove gases at any stage in the engine cycle[92] showed that in the combustion occurring in the knocking zone prior to the passage of the flame, aldehydes and substances behaving as peroxides were formed. The quantity of the latter increased with greater knock intensity and decreased when tetraethyl lead was added to the fuel. Incorporation of aldehydes with the fuel did not affect the knock tendency nor the amount of peroxides formed. The latter were subsequently found to be largely nitrogen peroxide with small percentages of organic peroxides. The main source responsible for the formation of nitrogen peroxide was believed to be the hot active surface of the exhaust valve of the engine rather than the flame itself. Knocking was attributed to the disruptive explosion of intermediate oxidation products by branched-chain reactions.[93]

Ubbelohde,[94] in formulating a mechanism for the combustion of paraffin hydrocarbons, assumed that the chain carriers must be of a nature similar to those involved in the combustion of aldehydes and ethers. Engine knocking was thought to be related to reactions of paraffins of more than 3 or 4 carbon atoms during combustion in the low-temperature region (250-320°C.). The chain reaction for aldehydes involves two carriers which are considered of great importance in the combustion of hydrocarbons.

$$\mathrm{RC({=}O)}\text{—} + \mathrm{O_2} \longrightarrow \mathrm{RC({=}O)OO}\text{—}$$
$$\mathrm{RC({=}O)OO}\text{—} + \mathrm{RC({=}O)H} \longrightarrow \mathrm{RC({=}O)OOH} + \mathrm{RC({=}O)}\text{—}$$

In the combustion of paraffins, each hydrocarbon molecule first undergoes partial dehydrogenation, as for example by the action of the aldehyde peroxide radical.

$$\mathrm{RC({=}O)OO}\text{—} + \mathrm{RCH_3} \longrightarrow \mathrm{RC({=}O)OOH} + \mathrm{RCH_2}$$
$$\mathrm{RCH_2} + \mathrm{O_2} \longrightarrow \mathrm{RCH_2O_2}$$
$$\mathrm{RCH_2O_2} + \mathrm{RCH_3} \longrightarrow \mathrm{RCH_2OOH} + \mathrm{RCH_2}$$

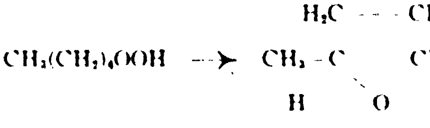
Other possibilities in this chain reaction are that the alkyl hydroperoxide can rearrange to an aldehyde and water.

$$\mathrm{RCH_2OOH} \longrightarrow \mathrm{RCHO} + \mathrm{H_2O}$$

or decomposition may take place,

$$\mathrm{RCH_2OOH} \longrightarrow \mathrm{RCH_2O}\text{—} + \text{—}\mathrm{OH}$$

Also, when the higher paraffins are involved, formation of oxygen ring compounds may occur:



In the oxidation of *n*-heptane with air[95] the initial stage of reaction was found to begin at 252°C. and to reach a maximum at 370°C. This initial stage was found to consist chiefly in the formation and decomposition of peroxides, including hydrogen peroxide and compounds of the type $HOCH_2O_2R$. At 110-115°C. the peroxides yielded ketones, aldehydes, alcohols, acids and carbon monoxide and dioxide. Gasolines containing appreciable percentages of aromatic hydrocarbons are said to have a smaller tendency to form peroxides than have pure hydrocarbons during combustion. Also, it is reported that the addition of from 0.2 to 2 per cent of aromatic hydroxy or amino compounds will inhibit or prevent peroxide formation in a gasoline during oxidation.[96] Ethanol, methanol and benzene have been found to exert a similar effect.[97]

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[92] A. Egerton, F. L. Smith and A. R. Ubbelohde, *Phil. Trans. Roy. Soc. (London)*, 1935, **234**, 433; *Chem. Abs.*, 1935, **29**, 8305, *Brit. Chem. Abs.* **B**, 1936, 7; *J. Inst. Pet. Tech.*, 1935, **21**, 403A.

[93] A. R. Ubbelohde, J. W. Drinkwater and A. Egerton, *Proc. Roy. Soc. (London)*, 1935, **A153**, 103; *Chem. Abs.*, 1936, **30**, 2358; *Brit. Chem. Abs.* **B**, 1936, 356. A. Egerton and A. R. Ubbelohde, *Nature*, 1935, **135**, 997; A. R. Ubbelohde and A. Egerton, *ibid.*, 67; *Chem. Abs.*, 1936, **30**, 2358, 3649; *Brit. Chem. Abs.* **A**, 1935, 937; 1936, 356. *J. Inst. Pet. Tech.*, 1935, **21**, 253A. See also M. Precoul, *Rev. petrolifere*, 1936, **696**, 1285.

[94] A. R. Ubbelohde, *Proc. Roy. Soc. (London)*, 1935, **A152**, 354; *Chem. Abs.*, 1936, **30**, 2167; *Brit. Chem. Abs.* **A**, 1936, 294. *Z. Elektrochem.*, 1936, **42**, 468; *Chem. Abs.*, 1936, **30**, 6920.

[95] K. I. Ivanov and V. K. Savinova, *J. Applied Chem. (U.S.S.R.)*, 1935, **8**, 64; *Chem. Abs.*, 1935, **29**, 6725; *Brit. Chem. Abs.* **A**, 1935, 937

Boerlage and Van Dyck[98] consider that detonation is the result of excessive compression during combustion. In an air-fuel mixture burning without detonation the flame progresses smoothly, but in a knocking combustion the last portion of the mixture, or "end gas," is compressed as a result of the advancing flame until a simultaneous explosive ignition occurs. This same type of reaction would occur if the original mixture were sufficiently compressed. Suggestions made for avoiding detonation were to cool the "end gas" or to increase the speed of travel of the compressing flame (e.g., by turbulence) so that the quantity of "end gas" exploding is negligible, owing to the fact that the chemical reactions leading to spontaneous ignition require time. It was believed that an important factor in hydrocarbon combustion is decomposition before reaction with oxygen.

Rice[99] also considered that there is probably a preliminary decomposition of hydrocarbons into smaller units, chiefly olefins and paraffins, partly from the thermal effect and partly from attack of molecular fragments on the original hydrocarbons. Since in thermal disruption one molecule is suddenly replaced by several smaller molecules, an extensive decomposition would have a two-fold result: (1) The pressure increase would be equivalent to raising the engine compression 5 to 25 per cent. (2) The rate of oxidation of the fuel would be greatly increased because of the larger number of fuel molecules per unit volume. Thus, the knocking tendency would be expected to be greater with an increasing number of moles of decomposition products per mole of original hydrocarbon. In this case an efficient antiknock compound would be one which would decrease the number of moles of decomposition product.

ANTIKNOCK OR KNOCK-SUPPRESSING COMPOUNDS

Although many of the substances which fall under this classification have received previous mention,[100] they are further discussed here because of their steadily increasing importance. The influence of the chemical nature of the fuel on the antidetonating power of the latter (expressed as octane number) was determined by Roberti[101] for a large number of the following: saturated hydrocarbons, olefins, aromatic hydrocarbons, naphthenes and others. These investigations disclosed that the resistance to detonation in the open-chain hydrocarbons decreased with increase in the number of carbon atoms, but increased in the presence of side chains and with compactness of the molecule. Double bonds were also found to aid the anti-detonating power, their influence being greater, the nearer the double bond was to the center of the molecule. Although cyclization increased the octane number, the addition of small quantities of such compounds as lead tetraethyl or iron carbonyl increased considerably the ability of the hydrocarbons as anti-detonants.

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[96] C. Candea and N. Cristodulo, *Chimie et industrie*, 1934, **31** (*April Special No.*), 374; *Chem. Abs.*, 1934, **28**, 5972; *Brit. Chem. Abs.* **B**, 1934, 662.

[97] G. Roberti, *Gazz. chim. ital.*, 1934, **64**, 564; *Chem. Abs.*, 1935, **29**, 1615; *Brit. Chem. Abs.* **B**, 1934, 1092.

[98] G. D. Boerlage and W. J. D. van Dyck, *Proc. Inst. Automobile Eng.*, 1934, **28**, 366; *J. Inst. Pet. Tech.*, 1935, **21**, 40; *Chem. Abs.*, 1934, **28**, 6290; 1935, **29**, 3502; *Brit. Chem. Abs.* **B**, 1934, 309; 1935, 342. G. D. Boerlage and A. J. van Peski, *Chem. Weekblad.*, 1934, **31**, 700; *Chem. Abs.*, 1935, **29**, 3502.

[99] F. O. Rice, *Ind. Eng. Chem.*, 1934, **26**, 259; *Chem. Abs.*, 1934, **28**, 6990; *Brit. Chem. Abs.* **B**, 1934, 486; *J. Inst. Pet. Tech.*, 1934, **20**, 235A.

[100] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Company, Inc., New York, 1934.

[101] G. Roberti, *Energi termica*, 1935, **3** (3), 60; *Chem. Abs.*, 1935, **29**, 7627. For a discussion of the importance of the composition of upper-cylinder lubricants and antiknock agents for internal-combustion engines see C. Becher Jr., *Seifensieder-Ztg.*, 1934, **61**, 584; *Chem. Abs.*, 1934, **28**, 7494. The loss in antiknock properties of gasoline upon acid treatment is discussed by C. Wirth III, E. R. Kanhofer and G. B. Murphy, *Oil Gas J.*, 1933, **32** (8), 13; *Chem. Abs.*, 1933, **27**, 5526.

The effect of the addition of 10 to 20 per cent of benzene, toluene, or either methyl, ethyl, propyl, butyl, isobutyl or isoamyl alcohol to gasoline was studied by Aubert and Duchene.[102] They reported that detonation was retarded by these substances up to 145°C. From 148° to 154°C. benzene and toluene seemed to have little effect, although the alcohols remained still active. Of the pure hydrocarbons with which Aubert and Duchene worked, hexane gave auto-ignition, 3-methylpentane and isohexane detonated to some extent, and 2,3-dimethylbutane was found to be inert. Further studies revealed that cyclohexene and cyclohexadiene showed auto-ignition whereas 1-hexene and cyclohexane were resistant to detonation. The injection of ethyl or methyl alcohol with fuel acts as a regulator and completely suppresses knocking, according to Aubert, Clerget and Duchene[103] who proposed this for the combustion of heavy oils. They also suggested that benzyl alcohol, benzoic and oenanthylic aldehyde may be substituted for the alcohols previously mentioned.

The use of isopentane[104] and isopropyl ether[105] in amounts constituting 30 per cent by weight of the non-knocking fuel has been described. Another fuel[106] is that obtained by cracking methane and its gaseous homologues. In one instance the product thus secured contained 8 volumes of propane plus butene, 32 volumes of ethylene, 11.6 volumes of hydrogen, 11 volumes of ethane plus propane and 1.2 volumes of nitrogen.

Some of the more interesting aromatic compounds suggested are: those of the benzene series which have been converted to nitrogen bases by heating under pressure and at elevated temperatures in the presence of ammonia gas,[107] alkylated compounds formed by treating gasoline with olefins in the presence of preformed acid sludge derived from the treatment of hydrocarbon material with sulphuric acid,[108] esters of a dibasic acid such as butyl oxalate or butyl phthalate or other mono or diakyl oxalate or phthalate,[109] benzene or acetone solutions of nitro compounds of aniline,[110] e.g., tetranitromethylaniline or hexanitrodiphenylamine and terpenes (e.g., pinene, terpineol, or camphor). Tetralin peroxide[111] has been used also, especially in Diesel fuels. Pyzel[112] suggests a motor fuel for compression ignition engines to which has been added a mineral oil insoluble in liquid sulphur dioxide and of which an appreciable portion boils below 400°C.

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[102] M. Aubert and R. Duchene, *Compt. rend. 3me congr. chauffage ind., Chaleur et ind.*, 1934, **15** (169), 1416; *Chem. Abs.*, 1934, **28**, 7505; *Brit. Chem. Abs.* **B**, 1935, 614.

[103] M. Aubert, P. Clerget and R. Duchene, *Chimie et industrie*, 1935, **33**, 811; *Chem. Abs.*, 1935, **29**, 5256; *Brit. Chem. Abs.* **B**, 1935, 614. For the use of alcohol as an antiknock material see E. Endo, *J. Fuel Soc., Japan*, 1934, **13**, 992; *Chem. Abs.*, 1934, **28**, 7505; *J. Inst. Pet. Tech.*, 1934, **20**, 567A.

[104] F. B. Neptune, H. M. Trimble and R. C. Alden, *Nat. Petroleum News*, 1936, **28** (19) 25, 28, 30; *Chem. Abs.*, 1936, **30**, 6177; *J. Inst. Pet. Tech.*, 1936, **22**, 353A; *Oil Gas J.*, 1936, **34** (49), 26; *Chem. Abs.*, 1936, **30**, 5401

[105] H. E. Buc, U. S. P. 2,046,243, June 30, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 5768. British P. 445,503, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 312A; *Chem. Abs.*, 1936, **30**, 6925.

[106] P. Feiler, German P. 602,584, 1934 to I. G. Farbenind. A. G.; *Chem. Abs.*, 1935, **29**, 920.

[107] G. Egloff and R. E. Schaad, U. S. P. 1,994,243, March 12, 1935 to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 3150, *Brit. Chem. Abs.* **B**, 1936, 265.

[108] V. N. Ipatieff, U. S. P. 2,001,910, May 21, 1935 to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 4573; *Brit. Chem. Abs.* **B**, 1936, 486.

[109] G. F. Ruddies, U. S. P. 1,980,097, Nov. 6, 1934; *Chem. Abs.*, 1935, **29**, 334; *Brit. Chem. Abs.* **B**, 1935, 892.

[110] Y. Ueda, Japanese P. 113,623, 1935; *Chem Abs.*, 1936, **30**, 3622. See also Dutch P. 59,105, 1931 to Fuel Development Corp.; *J. Inst. Pet. Tech.*, 1935, **21**, 99A. J. F. P. de la Riboisiere, U. S. P. 1,982,420, Nov. 27, 1934; *Chem. Abs.*, 1935, **29**, 595. E. F. Pevere, U. S. P. 2,021,088, Nov. 12, 1935 to Texas Co.; *Brit. Chem. Abs.* **B**, 1936, 778; *Chem Abs.*, 1936, **30**, 606.

[111] F. R. Moser, U. S. P. 2,011,297, Aug. 13, 1935 to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 6736; British P. 421,928, 1935, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1935, **29**, 4572; *Brit. Chem. Abs.* **B**, 1935, 216.

Many organo-metallic compounds have been investigated as anti-detonants. Some of those which have been reported are: lithium[113] or thallium alkyls or aryls, e.g., primary butyl lithium, organic ditellurides[114] such as diphenylene ditelluride, selenium compounds, for example, phenyl diselenocyanate[115] and also organic derivatives of metallocyanic acids, exemplified by the tetraisopropyl ester of hydroferrocyanic acid.[116] The use of the copper, nickel, and cobalt[117] compounds of salicylalallylamine, salicylalmethylamine, β-naphtholallylamine, protocatechualethylamine and the condensation products of allylamine and acetylacetone have also been considered as antiknock agents. Employment of various lead alkyls has been proposed by Voorhees.[118]

Other substances which have been recommended are polymerized nickel carbonyl,[119] and iron carbonyl.[120] To this latter compound are usually added compounds containing oxygen or nitrogen, as for example, toluidine or quinone,[121] soluble organic compounds of the benzene series, isobutyl alcohol, aldehydes or ketones[122] and monomethylaniline or dimethylaniline.[123] Danner[124] suggests incorporation of a small proportion of a metallic nitrosocarbonyl, e.g., cobalt nitrosocarbonyl, to the hydrocarbon fuel oil to reduce knocking. A mixture of the chlorides of uranium and vanadium dissolved in acetone has also been proposed.[125]

Another organo-metallic compound whose importance is widely recognized is tetraethyl lead. The effectiveness of this substance in increasing the critical compression ratio of individual hydrocarbons has been studied by Campbell, Signaigo,

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[112] D. Pyzel, Canadian P. 346,022, 1934, to Shell Development Co.; *Chem. Abs.*, 1935, **29**, 2350.

[113] R. de M. Taveau, U. S. P. 1,991,127, Feb. 12, 1935 to Texas Co.; *Brit. Chem. Abs.* **B**, 1936, 87; *Chem. Abs.*, 1935, **29**, 2349. S. F. Birch, *J. C. S.*, **1934**, 1132; *J. Inst. Pet. Tech.*, 1934, **20**, 523A; *Chem. Abs.*, 1934, **28**, 6423.

[114] E. F. Pevere, U. S. P. 1,991,333, Feb. 12, 1935, to Texas Co.; *Brit. Chem. Abs.* **B**, 1936, 87; *Chem. Abs.*, 1935, **29**, 2349; Canadian P. 347,588, 1935 to Texaco Development Corp.; *Chem. Abs.*, 1935, **29**, 3150.

[115] L. Rosenstein and W. J. Hund, U. S. P. 1,920,766, Aug. 1, 1933 to Shell Development Co.; *Brit. Chem. Abs.* **B**, 1934, 311; *Chem. Abs.*, 1933, **27**, 4918. For use of small proportions of cyanamide, cyanic acid, cyanoanilide, dicyanodiamide, urea or hydrazine see R. Cross, U. S. P. 1,958,744, May 15, 1934; *Chem. Abs.*, 1934, **28**, 4591; *Brit. Chem. Abs.* **B**, 1935, 261.

[116] L. Rosenstein, U. S. P. 1,948,449, Feb. 20, 1934 to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 2891.

[117] French P. 742,957, 1933, to N. V. de Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1933, **27**, 3812. German P. 582,718, 1933; *Chem. Abs.*, 1934, **28**, 890. See also Dutch P. 30,503, 1933; *Chem. Abs.*, 1933, **27**, 5961. German P. 594,557, 1934; *Chem. Abs.*, 1934, **28**, 4591. N. Max, U. S. P. 2,023,142 and 2,023,372, Dec. 3, 1935, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 850, 1552. Canadian P. 356,194, 1936; *Chem. Abs.*, 1936, **30**, 2747.

[118] V. Voorhees, U. S. P. 1,974,167, Sept. 18, 1934 to Standard Oil Co. of Indiana; *Brit. Chem. Abs.* **B**, 1935, 713; *Chem. Abs.*, 1934, **28**, 6997. See also F. W. Sullivan Jr. and V. Voorhees, U. S. P. 1,938,546, Dec. 5, 1933 to Standard Oil Co. of Indiana; *Chem. Abs.*, 1934, **28**, 1182; *Brit. Chem. Abs.* **B**, 1934, 918. F. W. Sullivan, Jr. and F. F. Diwoky, U. S. P. 1,938,547, Dec. 5, 1933 to Standard Oil Co. of Indiana; *Chem. Abs.*, 1934, **28**, 1182; *Brit. Chem. Abs.* **B**, 1934, 918. The use of a hydrocarbon derivative of a metal containing a dimethyl group such as lead, thallium or nickel compounds or dimethyldiamyl lead has been recommended by G. Alleman, U. S. P. 1,940,439, Dec. 19, 1933 to Sun Oil Co.; *Chem. Abs.*, 1934, **28**, 1523; *Brit. Chem. Abs.* **B**, 1934, 919. For use of vaporized metals such as lead to inhibit detonation see E. Rector, U. S. P. 1,989,113, Jan. 29, 1935 to Rector Gasifier Co.; *Chem. Abs.*, 1935, **29**, 1978.

[119] H. G. Webster, U. S. P. 2,002,805, May 28, 1935 one half to J. W. G. Wennett; *Chem. Abs.*, 1935, **29**, 4932.

[120] M. J. Leahy, *Refiner*, 1935, **14**, 82; *Brit. Chem. Abs.* **B**, 1935, 1031; *J. Inst. Pet. Tech.*, 1935, **21**, 178A; *Chem. Abs.*, 1935, **29**, 2721.

[121] W. Gaus, German P. 508,917, 1933 to I. G. Farbenind. A. G.; *Chem. Abs.*, 1934, **28**, 1181.

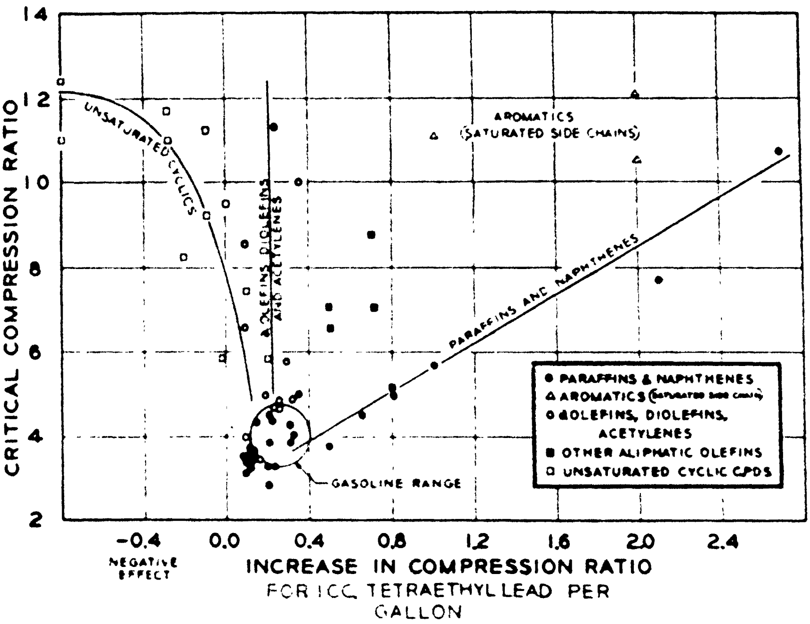
[122] W. Wilke, E. Kuss and G. Retter, German P. 518,232, 1933, to I. G. Farbenind. A. G.; *Chem. Abs.*, 1934, **28**, 1181.

[123] M. Mueller-Cunradi and W. Wilke, U. S. P. 1,940,096, Dec. 19, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1523. See also British P. 334,181, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, **25**, 1070.

[124] P. S. Danner, U. S. P. 1,954,863, April 17, 1934, to Standard Oil Co. of California; *Brit. Chem. Abs.* **B**, 1935, 216; *Chem. Abs.*, 1934, **28**, 3888.

[125] A. Pacyna, U. S. P. 1,973,320, Sept. 11, 1934; *Chem. Abs.*, 1934, **28**, 6997; *Brit. Chem. Abs.* **B**, 1935, 759.

Lovell and Boyd.[126] Paraffins, olefins, naphthenes, aromatics and unsaturated cyclic hydrocarbons were investigated and critical compression ratios were plotted against increases in compression for an addition of 1 cc. of tetraethyl lead per gallon. This is shown graphically in Fig. 240. In this instance the minus sign indicates that addition of the lead compound caused an increase in knock intensity or decrease in compression ratio for border-line or incipient knock. In using Fig. 240, one must remember that the lines passing through the points of different classifications do not necessarily represent functions nor do they have any absolute significance. There is also indicated an area representative of an approximate location of commercial gasolines. Since this area is relatively small, values of 0.1 to 0.3 ratio per cc. might be contrasted with values ten times as great for certain aromatic, paraffin, and naphthene hydrocarbons. The line drawn roughly through the paraffin and naphthene hydrocarbons may indicate that lead is progressively more effective in those materials of higher antiknock value. However, in the case of such compounds as alpha-olefins, diolefins and acetylene homologues, the line through their classification is noted to be nearly vertical. In other words, the effectiveness of lead



Courtesy Industrial and Engineering Chemistry

FIG. 240.—Comparison of Critical Compression Ratios of Hydrocarbons with Increase in Compression Ratio on Addition of Tetraethyl Lead. (J. M. Campbell, F. K. Signaigo, W. G. Lovell and T. A. Boyd)

shows little variation irrespective of the critical compression ratios of the hydrocarbons under consideration. A line showing the location of certain unsaturated cyclic compounds such as cyclopentadiene derivatives and as well, certain aromatics with unsaturated side chains, indicates a progressive lowering of the effectiveness of lead in them with increase in the critical compression ratios of the compounds. In a few rare instances lead has a "negative" effect, that is, tetraethyl lead acts as a knock inducer and the critical compression ratio is lowered by the addition of the lead compound.

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[126] J. M. Campbell, F. K. Signaigo, W. G. Lovell and T. A. Boyd, *Ind. Eng. Chem.*, 1935, **27**, 593; *Chem. Abs.*, 1935, **29**, 4560; *Brit. Chem. Abs.* **B**, 1935, 614; *J. Inst. Pet. Tech.*, 1935, **21**, 254A. For the use of tetraethyl lead in aircraft fuels see F. R. Banks, *J. Roy. Aeronaut. Soc.*, 1934, **38**, 309; *Brit. Chem. Abs.* **B**, 1936, 728; *J. Inst. Pet. Tech.*, 1934, **20**, 468A; *Chem. Abs.*, 1935, **29**, 6412. The effect of metallic (lead) dope on the carbonization of oil in the combustion space of an engine is discussed by R. O. King, *Engineering*, 1933, **136**, 183; *Chem. Abs.*, 1933, **27**, 5526; *Brit. Chem. Abs.* **B**, 1933, 948. For pellet method of adding tetraethyl lead to motor fuels see P. Poetschke, U. S. P. 2,018,570, Oct. 22, 1935; *Brit. Chem. Abs.* **B**, 1936, 630; *Chem. Abs.*, 1936, **30**, 281.

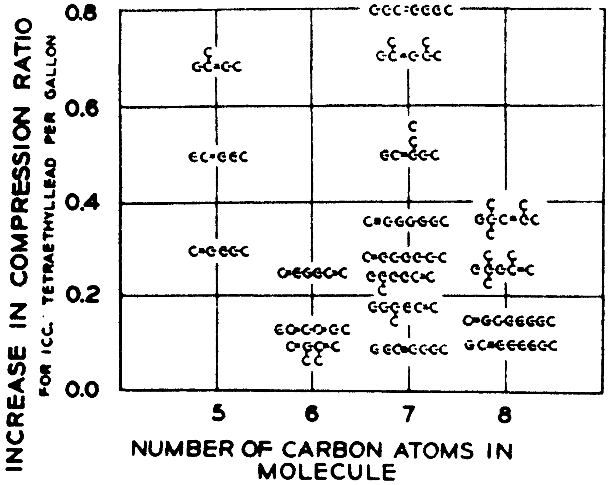


FIG. 241.
Influence of Structure of Aliphatic Unsaturated Hydrocarbons on Effectiveness of Tetraethyl Lead. (J. M. Campbell, F. K. Signaigo, W. G. Lovell and T. A. Boyd)

Courtesy Industrial and Engineering Chemistry

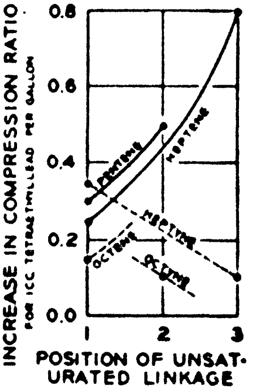


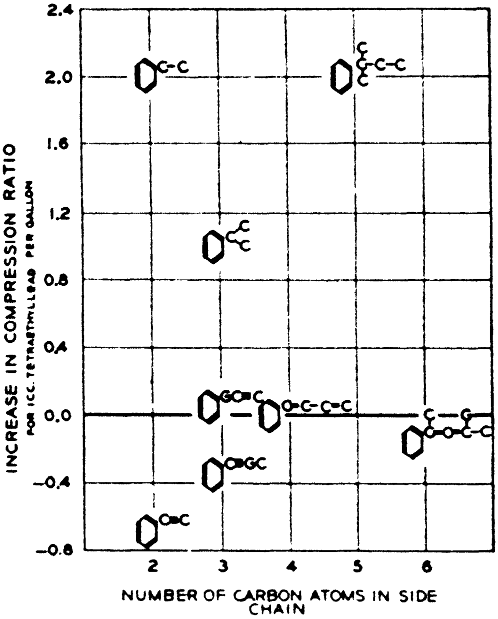
FIG. 242.
Effect of Position of Unsaturated Linkage on Result of Adding Tetraethyl Lead to Hydrocarbons. (J. M. Campbell, F. K. Signaigo, W. G. Lovell and T. A. Boyd)

Courtesy Industrial and Engineering Chemistry

Results of further investigations of the relationship of structure and lead effectiveness are also shown graphically in Fig. 241 giving data obtained on the aliphatic double- and triple-bonded compounds. For convenience, the effectiveness of lead (as measured by the increase in the critical compression ratio) has been plotted against the number of carbon atoms in the molecule. The compounds in which lead is more effective appear to be those which have a double bond removed from the end of the molecule. In Fig. 242 the effectiveness of lead in the compound has been plotted against the position of the unsaturated linkage for the pentenes and some heptenes and heptynes. Although the data were incomplete they do indicate that as the double bond moved toward the center of the molecule the effectiveness of lead in the compound increased. Fig. 243, for benzene rings with hydrocarbon

FIG. 243.
Influence of Side Chains of Benzene Ring on Effectiveness of Tetraethyl Lead. (J. M. Campbell, F. K. Signaigo, W. G. Lovell and T. A. Boyd)

Courtesy Industrial and Engineering Chemistry



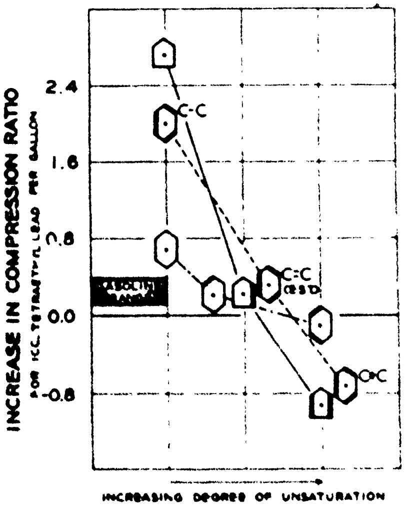


FIG. 244.
Effect of Double Bonds in Cyclic Compounds as Regards Addition of Tetraethyl Lead. (J. M. Campbell, F. K. Signaigo, W. G. Lovell and T. A. Boyd)

Courtesy Industrial and Engineering Chemistry

side chains, shows that for the saturated side chain the lead is most effective although with unsaturation of the side chain there is a decrease in the lead respondency. Those compounds which contained a triple bond in what might be called a "conjugated" position to the benzene ring exhibited a negative lead effect, and the hydrocarbon 1-phenyl-1,3-butadiene appeared unaffected by lead. In Fig. 244 these latter relationships are presented, thus showing the effect of the successive introduction of double bonds into some cyclic compounds. In the series cyclohexane, cyclohexene and cyclohexadiene, the effect of the lead becomes progressively less and eventually negative. Similar relationships were observed in the series cyclopentane, cyclopentene and cyclopentadiene. Other investigations were also carried out with ethylbenzene and phenylethylene. Tetraethyl lead affected the critical compression ratios of a few hydrocarbons greatest at low concentrations as shown in Fig. 245.

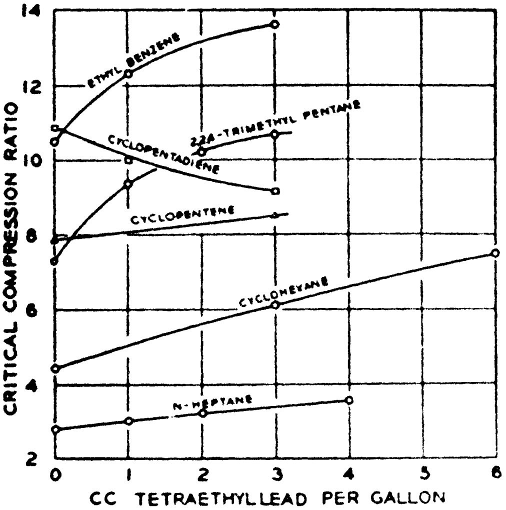


FIG. 245. Comparison of Tetraethyl Lead Concentration and Critical Compression Ratio for Various Hydrocarbons. (J. M. Campbell, F. K. Signaigo, W. G. Lovell and T. A. Boyd)

Courtesy Industrial and Engineering Chemistry

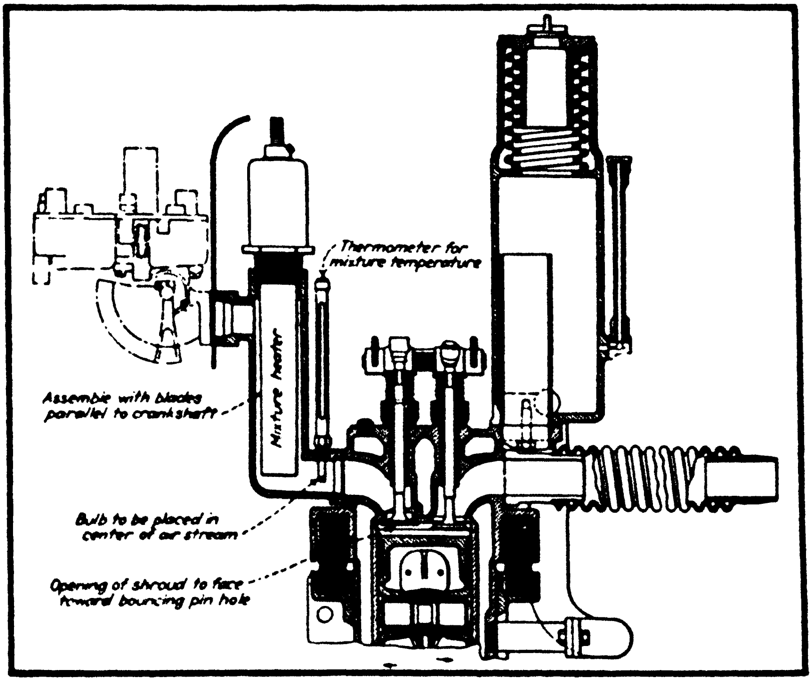
The thermal decomposition of tetraethyl lead in benzene solution, both in the absence and presence of ethylene and hydrogen, has been studied by Cramer.[127] He found that although two hours were required to complete the reaction at 240-275°C., the presence of methane gas was not detected; the paraffin fraction consisted of ethane with small amounts of butane. The liquid reaction products (in addition to benzene) were light colored oils and were believed to be derived from the tetraethyl lead and added ethylene. Cramer noted with few exceptions close agreement between the determined and calculated values for the liquid reaction products. He further concluded that these reactions are largely independent of wide variation in pressures, as well as relatively small temperature differences. It was also observed that practically the same amounts of unreacted ethylene were obtained from widely varying proportions of tetraethyl lead and ethylene. Attempts to decom-

[127] P. L. Cramer, *J.A.C.S.*, 1934, **56**, 1234; *Chem. Abs.*, 1934, **28**, 4376; *J. Inst. Pet. Tech.*, 1934, **20**, 407A; *Brit. Chem. Abs.* **A**, 1934, 761. See also J. A. Leermakers, *J.A.C.S.*, 1933, **55**, 4508 *Chem. Abs.*, 1934, **28**, 739; *J. Inst. Pet. Tech.*, 1934, **20**, 26A; *Brit. Chem. Abs.* **A**, 1934, 34. For the catalytic decomposition of lead tetraphenyl see M. Koton, *J.A.C.S.*, 1934, **56**, 1118; *J. Inst. Pet. Tech.*, 1934, **20**, 407A; *Chem. Abs.*, 1934, **28**, 3721; *Brit. Chem. Abs.* **A**, 1934, 738. The photolysis of lead tetramethyl and lead tetraphenyl are discussed by P. A. Leighton and R. A. Mortensen, *J.A.C.S.*, 1936, **58**, 448; *J. Inst. Pet. Tech.*, 1936, **22**, 25A; *Chem. Abs.*, 1936, **30**, 3327.

pose any quantity of tetraethyl lead in the absence of a solvent gave very inconsistent results.

MEASUREMENT OF KNOCK RATING

Although a detailed discussion of the test engines, reference fuels and procedures used for the determination of knock rating, or anti-detonating value, for various fuels and fuel mixtures is beyond the scope of this book, nevertheless because of the vast amount of work which has been done on the standardization of procedures and equipment, some mention of these is not out of place. The question[128] of standardization of test methods and equipment received little consideration until 1928 when (in the United States) the Co-operative Fuel Research Committee undertook the development of a uniform test method. This work has been carried out in conjunction with interested groups in England, Germany, France and Holland.[129] Horning[130] points out that the popularity of the Co-operative Fuel


Thermometer for mixture temperature
Assemble with blades parallel to crankshaft
Mixture heater
Bulb to be placed in center of air stream
Opening of shroud to face toward bouncing pin hole

Courtesy Industrial and Engineering Chemistry

FIG. 246.—Sectional View of Engine Cylinder Head for C. F. R. Motor Method of Knock Rating Measurement. (L. C. Lichty and E. J. Ziurys)

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[128] C. H. Barton, C. H. Sprake and K. Stansfield, *Proc. World Petroleum Congr., London*, 1933, **2**, 133; *Chem. Abs.*, 1934, **28**, 4880.

[129] An account of the activities of the committee and the development of a method for determining the octane number of motor fuels has been given by T. A. Boyd and C. B. Veal, *Proc. World Petroleum Congr., London*, 1933, **2**, 139; *Chem. Abs.*, 1934, **28**, 4880; *Brit. Chem. Abs.* **B**, 1934, 743; *J. Inst. Pet. Tech.*, 1934, **20**, 301A.

[130] H. L. Horning, *J. Soc. Automotive Eng.*, 1931, **26**, 436. See also C. Bonnier, *Ann. combustibles liquides*, 1934, **9**, 19; *J. Inst. Pet. Tech.*, 1934, **20**, 301A for a description of the C. F. R. engine and method of testing.

Research (C.F.R.) engine may be attributed to its universality, ruggedness and relatively low cost.

Reference Standards Used in the Measurement of Motor Knock. The relative tendencies to knock in an engine have been measured by Lovell and co-workers[131] for naphthene hydrocarbon-gasoline mixtures. The results were expressed in terms of the aniline equivalent[132] which was defined as the number of centigram-moles of aniline that must be added to a reference fuel to make 1000 cc. of a fuel equivalent in knocking tendency to a molal solution of the hydrocarbon in the reference gasoline, provided the hydrocarbon knocked less than the reference fuel. When the hydrocarbon knocked more than the reference fuel the aniline equivalent was the number of centigram-moles of aniline added to a 1-molal solution of the hydrocarbon in the reference gasoline to make a fuel that was equivalent in knocking tendency to the reference gasoline. Further investigations[133] were made on hydrocarbons of the aromatic series alone and in admixture with gasoline. The measurements of the tendency of these substances to knock was carried out in a single-cylinder, variable-compression engine equipped with an evaporative cooling system and fitted with a bouncing-pin indicator. The results expressed in aniline equivalents, some of which are listed in Table 197, are for mixtures of the hydrocarbon with gasoline.

TABLE 197.—*Effect of Structure on Resistance to Knocking*

Hydrocarbon	Aniline Equivalent	Hydrocarbon	Aniline Equivalent
Cyclopentadiene	34	Phenylethylene	20
Dicyclopentadiene	65	Ethylbenzene	19
Dimethylfulvene	61	3-Phenylpropyne	8
Methylphenylfulvene	36	1,2-Methylethylbenzene	15
1,3-Cyclohexadiene	39	Pseudocumene	20
1,4-Cyclohexadiene	29	Tetrahydronaphthalene	19

Other experiments[134] were made using a wider variety of pure hydrocarbons. Comparisons were then made on the basis of the compression ratio for border-line or incipient knock in a single-cylinder variable-compression engine. This compression or "critical compression ratio," is defined as that at which knock becomes just audible in a quiet room when the engine is running at full load, engine speed 600 r.p.m., jacket water boiling, no external heat applied to mixture, mixture ratio for maximum power and spark timing for maximum power. The results so obtained, some of which are reported in Table 198, will of course vary in some instances with changes in the conditions under which the engine is run.

The data appeared to indicate that for the aliphatics there is an increasing tendency to knock with increasing length of the carbon chain as illustrated by Fig. 247, methane showing the least tendency. Saturated cyclic hydrocarbons exhibit even greater tendency to knocking than do the corresponding aromatic hydrocarbons, though less than for paraffins. Cyclohexane derivatives for the most part are comparable with many commercial gasolines in detonation qualities. Although two and three double bonds within the ring exert a strong antiknock effect, a solitary double bond produces comparatively little effect. Cyclopentene was noted to knock

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[131] W. G. Lovell, J. M. Campbell and T. A. Boyd, *Ind. Eng. Chem.*, 1933, **25**, 1107; *Chem. Abs.* 1933, **27**, 5955.

[132] W. G. Lovell, J. M Campbell and T. A. Boyd, *Ind Eng. Chem*, 1931, **23**, 26. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York 1934.

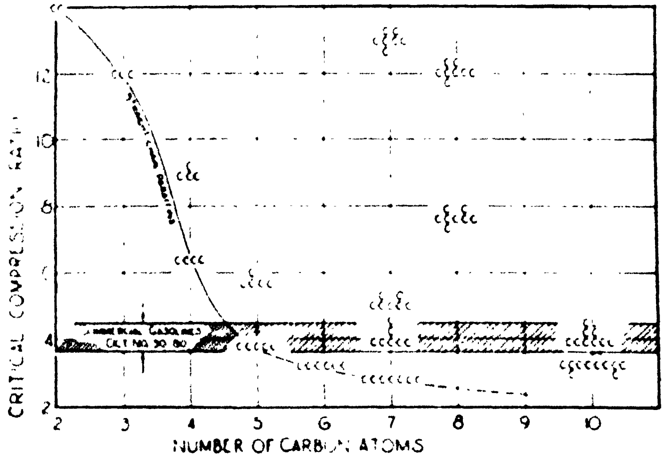
[133] W. G. Lovell, J. M. Campbell, F. K. Signaigo and T. A. Boyd, *Ind. Eng. Chem.*, 1934, **26** 475; *Chem. Abs.*, 1934, **28**, 4880; *Brit. Chem. Abs.* **B**, 1934, 613; *J Inst. Pet. Tech*, 1934, **20**, 357A

[134] W. G. Lovell, J. M. Campbell and T. A. Boyd, *Ind. Eng. Chem*, 1934, **26**, 1105; *Chem. Abs.* 1934, **28**, 7505; *Brit. Chem. Abs.* **B**, 1935, 887; *J. Inst. Pet. Tech.*, 1934, **20**, 564A.

TABLE 198.—*Effect of Structure on Resistance to Knocking in Terms of Aniline Equivalents and Critical Compression Ratios*

Hydrocarbon	Aniline Equivalent	Critical Compression Ratio
Isopentane	9	5.7
3-Ethylpentane	4	3.9
2,4-Dimethylpentane	8	5.0
2,2,3-Trimethylpentane	17	12.0
3,4-Diethylhexane	0	3.9
1-Pentene	10	5.8
2,4-Hexadiene	29	6.6
3-Heptene	12	4.9
Cyclopentane	14	10.8
Ethylcyclopentane	1	3.9
Dipentene	23	5.9
Cyclohexane	7	4.5
Isopropylbenzene	22	11.9
Mesitylene	31	14.8
Trimethylphenylallene	36	8.3

more than cyclopentane although this was an exceptional case. An increase in the length of the side chain was observed to increase the tendency for knock in both the aromatics and naphthenes although branching of the side chain produced the opposite effect.



Courtesy Industrial and Engineering Chemistry

FIG. 247.—Critical Compression Ratios of Paraffin Hydrocarbons. (W. G. Lovell, J. M. Campbell and T. A. Boyd)

Another method of measuring knock rating is that of comparing the engine performance of the fuel with that of various mixtures of isooctane (2,2,4-trimethylpentane) and *n*-heptane. The octane number of a fuel is defined as the percentage of isooctane (the antiknock agent) in an isooctane-heptane blend which gives a knock tendency equal to that of the fuel tested.[135]

For the purpose of expressing the knock ratings of pure hydrocarbons in terms of octane numbers, Garner[136] and associates employed the term "blending octane number" as an index of the behavior of a hydrocarbon in altering the octane number of a reference fuel. Calculations were based on the assumption that a straight-line mixture relationship holds for blends of hydrocarbons and a reference fuel in concentrations up to about 25 per cent. Thus, a blend containing 15 per cent added pure hydrocarbon would be given a rating of 15 per cent of the octane number of the hydrocarbon plus 85 per cent of the value of the reference fuel. Although "blending octane numbers" are not exactly the same as actual octane numbers they give an indication of the effectiveness of a hydrocarbon as an antiknock. For paraffins and naphthenes the two types of ratings were found to be approximately the same, but the blending octane numbers of aromatics were lower and those of olefins were higher than the actual octane numbers.

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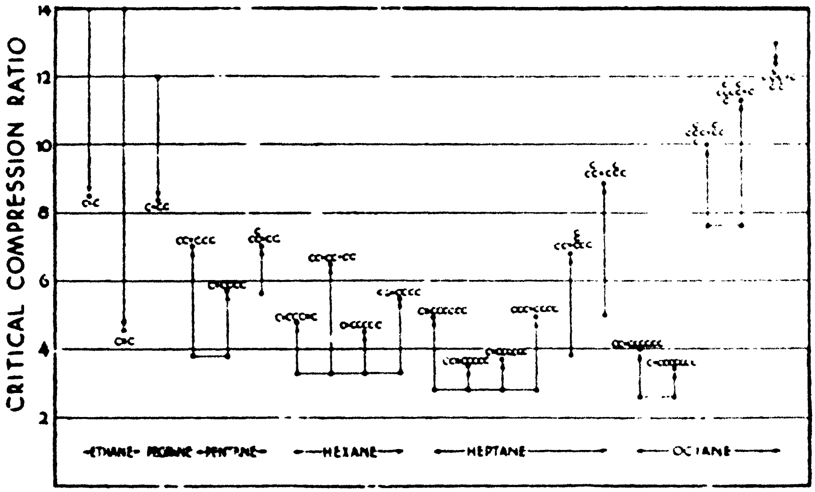
[135] F. H. Garner, R. Wilkinson and A. W. Nash, *J.S.C.I.*, 1932, 51, 265T.



Courtesy Industrial and Engineering Chemistry

FIG. 248.—Comparison of Critical Compression Ratios of Unsaturates with the Corresponding Paraffin Hydrocarbons. (W. G. Lovell, J. M. Campbell and T. A. Boyd)

Neptune and Trimble,[137] investigating lower-boiling hydrocarbons, found that the octane numbers of the 4-carbon olefins are lower than their blending octane numbers. When blended with gasoline in equal proportion there is a greater difference between iso- and *n*-pentane than between iso- and *n*-butane. However, with incorporation of *n*- or isobutane to give finished products of the same vapor pressure, the same antiknock effectiveness was noted. Substitution of *n*- and isopentane for the corresponding butanes indicated that isopentane was the most effective antidetonant. Neptune and Trimble believe small proportions of 4-carbon hydrocarbons present in motor fuels have been responsible in some instances for improved antiknock properties. For 1-heptene[138] the knock rating was determined in a 20 per cent (vol.) blend and the blending octane number found to be 79.5. When the value of this compound was compared with that of representative 7-carbon atom hydrocarbons of other series, it was noted that the introduction of a double bond into the heptane molecule in the α-position increased the blending octane number. A triple bond in the same position further increased the blending octane number but not to so great an extent.

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[136] F. H. Garner, E. B. Evans, C. H. Sprake and W. E. J. Broom, *Proc. World Petroleum Congr., London*, 1933, **2**, 170; *Brit. Chem. Abs.* **B**, 1934, 743. For a discussion of results obtained in terms of "blending octane numbers" for a number of gasolines on the Japanese market see T. Suwa, *J. Fuel Soc. Japan*, 1935, **14**, 75; *Brit. Chem. Abs.* **B**, 1935, 887.

[137] F. B. Neptune and H. M. Trimble, *Oil Gas J.*, 1934, **32**, No. 51, 44, 48; *Chem. Abs.*, 1934, **28**, 5646; *J. Inst. Pet. Tech.*, 1934, **20**, 486A.

[138] A. R. Bowen, A. W. Nash and F. H. Garner, *Nature*, 1933, **132**, 410; *Chem. Abs.*, 1933, **27**, 5955.

Becker and Kass[139] report that although the most direct method of determining octane numbers is by comparison of samples with blends of isooctane and normal heptane, the cost of the latter prohibits their use in routine testing. As a substitute for these hydrocarbons, they suggest standard reference fuels having octane numbers of 44 and 76 as determined with a C.F.R. engine. The latter fuels are made from straight-run naphthas which are applicable for use in multicylinder engines.

A procedure for rating aviation fuels is that designated as the "Allowable Boost Ratio" method.[140] This is defined as the ratio of the boost pressure[140a] for the sample at incipient knock to the boost pressure for the standard (pure isooctane) at incipient knock. The reported advantages of this method are: the test conditions more closely approximate those of the supercharged aero engine, the scale has no upper limit, and the incipient knock is closer to practice than the heavy knock needed in the C.F.R. test.

In view of certain defects of the octane scale for rating motor fuels, Evans, Dodds and Garner[141] worked out a pressure scale based on the compression just under that at which knocking took place. This scale does not involve the peculiarities of behavior of fuels consequent upon their varying temperature susceptibilities, but at the same time it is easily correlated with the octane-heptane scale on any particular engine. The difficulties encountered in determining octane numbers from 85 to 100 by the C.F.R. motor method are avoided. Also the engine used in the latter operation is unsatisfactory for octane numbers above 85. The procedure, then, is to note incipient knock by ear or preferably by microphone or temperature plug; and to determine the pressure. From the latter value the octane number can be read off the calibration pressure-octane number curve previously established for the particular engine. Other methods that have been suggested are: an electromagnetic device for determining pressure variations which may be used to study knock in motors[142] and comparison of the utilizable powers of two gasolines. In the latter case, fuels are valued by their "synthetic indexes" which may be defined as the ratio of the maximum power produced by the gasoline to that produced by a standard fuel in a standard motor under definite conditions of temperature and compression, both fuels being fed at the knock limit and giving the same percentage of carbon monoxide in the exhaust.[143]

Relation Between Constitution and Antiknock Value of Hydrocarbons

It has been shown by Hofmann, Berlin and Schmidt[144] that cyclohexene and butadiene lose in antiknock properties upon being dimerized to dicyclohexene and dibutadiene. The octane ratings for cyclohexene and butadiene were 70-71 and 83-84, respectively, but after dimerization became 53-54 and 60-61, respectively. Further experiments carried out by Schmidt[145] also substantiate the work of Lovell, Campbell and Boyd (*q.v.*). Several of the paraffins, unsaturated hydrocarbons, naphthenes and aromatics were studied as well as the following alcohols: ethyl, *n*-propyl, *n*-butyl, isopropyl, isobutyl and isoamyl, and cyclohexanol and methylcyclohexanol. The results showed that paraffins as a class give the lowest and aromatics the highest octane numbers, while methyl groups in a branched chain and hydroxyl and amino radicals all raise the octane number. The 5-membered ring naphthenes gave higher octane numbers than the corresponding 6-membered compounds. It was also noted that the octane numbers of unsaturates decreased during storage except in the case of the aromatics with unsaturated side chains. With the monohydric alcohols the octane number became less with increasing molecular weight.

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[139] A. E. Becker and C. B. Kass, *Proc. World Petroleum Congr.*, *London*, 1933, **2**, 50; *J. Inst. Pet. Tech.*, 1934, **20**, 237A

[140] G. D. Boerlage, L. A. Peletier and J. L. Tops, *Aircraft Eng.*, 1935, **7**, 306; *J. Inst. Pet. Tech.*, 1936, **22**, 145A; *Chem. Abs.*, 1936, **30**, 1216

[140a] The pressure applied to the intake air

[141] E. B. Evans, E. M. Dodds and F. H. Garner, *J. Inst. Pet. Tech.*, 1935, **21**, 1000; *Chem. Abs.*, 1936, **30**, 3991; *Brit. Chem. Abs.* **B**, 1936, 133; *J. Inst. Pet. Tech.*, 1936, **22**, 54A

[142] C. Te Lou, *Compt. rend.*, 1934, **199**, 927; *Chem. Abs.*, 1935, **29**, 587

[143] M. Serruys, *Compt. rend.*, 1935, **201**, 815; *Brit. Chem. Abs.* **B**, 1936, 134; *Chem. Abs.*, 1936, **30**, 601.

[144] F. Hofmann, K. Berlin and A. W. Schmidt, *Brennstoff-Chem.*, 1933, **14**, 326; *Chem. Abs.*, 1933, **27**, 5955; *Brit. Chem. Abs.* **B**, 1933, 900.

Knock ratings of saturated and unsaturated hydrocarbons as determined by the C.F.R. Motor Method have been reported by Egloff.[146] Some of the values are listed in Table 199.

TABLE 199.—*Octane Ratings of Hydrocarbons.*

Hydrocarbon	Formula	Octane No.
Paraffins		
Methane	CH_4	125(Est.)
Ethane	C_2H_6	125(Est.)
Propane	C_3H_8	125(Est.)
Butane	C_4H_{10}	91
Isobutane	$CH_3CH(CH_3)CH_3$	99
Pentane	C_5H_{12}	64
2,2-Dimethylpropane	$CH_3C(CH_3)_2CH_3$	83
2-Methylbutane	$CH_3CH(CH_3)C_2H_5$	90
Hexane	C_6H_{14}	59
2,3-Dimethylbutane	$CH_3CH(CH_3)CH(CH_3)CH_3$	95
Heptane	C_7H_{16}	0
Octane	C_8H_{18}	0
2,2,4-Trimethylpentane	$CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$	100
Nonane	C_9H_{20}	−28
Isodecane	$C_{10}H_{22}$	93
Isododecane	$C_{12}H_{26}$	100
Olefins		
1-Butene	C_4H_8	80
2-Butene	C_4H_8	83
Isobutene	C_4H_8	87
Isobutene dimer	C_8H_{16}	84
Isobutene trimer	$C_{12}H_{24}$	87
Isoamylene dimer	$C_{10}H_{20}$	75
Cycloparaffins		
Methylcyclopentane	C_6H_{12}	82
Cyclohexane	C_6H_{12}	77
Aromatics		
Benzene	C_6H_6	97
Toluene	C_7H_8	100+

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[145] A. W. Schmidt, *Proc. World Petroleum Congr. London*, 1933, 2, 181; *J. Inst. Pet. Tech.*, 1934, 20, 301A; *Brit. Chem. Abs.* B, 1934, 915.

[146] G. Egloff, *Oil Gas. J.*, 1936, 35 (22), 58; *Chem. Abs.*, 1936, 30, 8588.

PROCEDURE USED FOR KNOCK-RATING DETERMINATIONS

A complete detailed description of these procedures will not be found here as this is beyond the scope of the book as previously mentioned, but an enumeration of methods will be made. The bouncing-pin method for the determination of knock rating has been widely used.[146a] Another procedure, described by Dumanois,[147] depends upon ascertaining the extra heat imparted to the cooling water when detonation occurs. The inlet and outlet cooling-water temperatures are measured for reference-fuel blends knocking respectively more and less than the fuel under test. The rating of the fuel under investigation is obtained by interpolation. Dumanois found that an increase of 10 per cent benzol in the reference fuel caused a decrease of 0.25°C. between inlet and outlet water temperatures.

MacCoull and Stanton[148] propose an electrical acoustic method for the measurement of engine knock. Oscillograms were taken of the knock disturbance, and measurements were made of the energy in various frequency bands. The C.F.R. standard engine developed a pronounced peak in knock energy at frequencies between about 6,000 and 7,000 cycles per second, while the L-head design of this same engine had a peak between 3,000 and 4,000 cycles per second.

MacCoull[149] reports that but little difference could be detected between the bouncing-pin and a throttle-audibility method,[150] when used in fuel matching, and therefore concluded no appreciable advantage exists for one method over the other in regard to accuracy. Some of the results are shown in Table 200.

TABLE 200. *Benzol Equivalents by Bouncing-Pin and Throttle-Audibility Methods on the Series-30 Ethyl Gasoline Corporation Engine.*

Tetraethyl Lead Content cc. per Gal.	Benzol Equivalent, Per Cent	
	Bouncing-Pin	Throttle-Audibility
1	13	16
2	30	31
3	38	38
4	44	46

FACTORS AFFECTING KNOCK-RATING DETERMINATION

It has been pointed out by Hubner and Murphy[151] that some automobile engines rate fuels higher in octane value than the Research (C.F.R.) Method while others rate the same fuels lower. After an examination of various types of engine design, it was shown that the inclined valve-in-head design with a central sparking plug gave the highest performance and best agreement with laboratory tests under cool running conditions such as those of the C.F.R. method.[152]

[146a] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. See also H. K. Cummings, *Proc. World Petroleum Congr.*, 1933, **2**, 193; *Brit. Chem. Abs.* **B**, 1934, 1046, for methods of specifying and measuring knock-ratings of aviation fuels. The development of testing methods for knock rating used in Japan with a discussion of the present standing of the methods has been reported by T. Suwa, *J. Fuel Soc., Japan*, 1933, **12**, 1358; *Chem. Abs.*, 1934, **28**, 1515; *J. Inst. Pet. Tech.*, 1934, **20**, 76A. For a review of methods of measuring antiknock characteristics of liquid fuels see also G. Roberti, *Ricerca sci.*, 1934, **5**, 405, *Brit. Chem. Abs.* **B**, 1936, 133.

[147] P. Dumanois, *Proc. World Petroleum Congr.*, 1933, **2**, 206; *J. Inst. Pet. Tech.*, 1934, **20**, 237A. See also A. W. Schmidt, *Automobiltech. Z.*, 1933, **36**, 493, *Chem. Abs.*, 1934, **28**, 1515.

[148] N. MacCoull and G. T. Stanton, *S.A.E. Journal*, 1936, **38**, 70.

[149] N. MacCoull, *S.A.E. Journal*, 1931, **26**, 467.

[150] Using both C.F.R. and Series-30 Ethyl Gasoline Corp. engines.

[151] W. H. Hubner and G. B. Murphy, *Proc. World Petroleum Congr., London*, 1933, **2**, 154; *J. Inst. Pet. Tech.*, 1934, **20**, 75A.

[152] For a discussion of correlation of Research Method ratings, A.S.T.M. rating and actual road tests see C. B. Veal, *S.A.E. Journal*, 1935, **36**, 165.

Schmidt and Seeber [153] studying the effect of various factors on detonation in a single cylinder engine with variable compression found that the octane number increased with richness of the gasoline-air mixture, but decreased with advanced ignition (over a range of 5° to 20°) as the air-intake and jacket temperatures rose.

The effect of temperature on knock-rating was studied by Peletier[154] who noted that increase of cooling liquid temperature in the test engines used resulted in an increase in knock intensity at otherwise equal conditions. In studying the knock-rating of various aviation fuels, Pye[155] observed that cylinder and gas temperatures are the most important variables in the operating conditions. Bonnier and Moynot[156] working with a C.F.R. motor showed that when knock was audible the temperature of the exhaust gases increased with the antiknock value of the fuel, the rate of increase being related directly to compression ratio. When there was no knock this temperature was approximately constant, but decreased with increased compression. Other investigations[157] by these workers further confirm their conclusions. Under non-detonating conditions, the exhaust temperature remained practically constant at a given compression ratio and mixture strength. The temperature they found normally fell with weakening of the mixture.

Brown and Marshall[158] report that for maximum fuel efficiency an engine should be run at a temperature just below the dew point of the fuel. Endo and Furuya[159] observed that when the inlet mixture temperature was high (150°C.), an "ethylized" fuel was better than one blended with benzol or ethyl alcohol. The antiknock property of standard fuels decreased as the temperature rose; the higher the octane number of the fuel the greater was the effect of temperature. Jacket and cylinder-head temperatures[160] were found to affect the relative knock-rating, while humidity and air temperature[161] affected the octane numbers of secondary detonation standards. Other factors which have been studied are: influence of carburetor setting and spark timing,[162] and the effect of sound intensity[163]

Relationships between the knocking power of light fuels and their physical properties have been investigated to some extent. For example, a correlation has been found between the octane number and the specific parachor of certain fuels.[164]

In the equation: $p = 1/d \times \sigma^{1/4}$, p = specific parachor, d = density and σ = surface tension. The parachor of a hydrocarbon is dependent upon its chemical constitution and is decreased by the presence of side chains, double bonds and ring structures. For hydrocarbons of the same boiling point a decrease in parachor was noted in the sequence: paraffin, unsaturated compounds, naphthenes and aromatics. The octane numbers of hydrocarbons were found to be inversely proportional to the parachor over the boiling point range 90-150°C. From a study of various benzines, these investigators also report that approximate determinations of the octane numbers can be made from relationships with physical constants other than the parachor. Marder[165] points out that the anti-detonating qualities are inversely related to the density (d_{20}) of the fuels.[165a] Fuels with high densities were more affected by changes in test conditions (in a given motor) than those of low density. Marder proposes that the parachor and density (d_{20}) may be used to correlate differences in octane numbers arising from different conditions of test.

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[153] A. W. Schmidt and F. Seeber, *Proc. World Petroleum Congr.*, *London*, 1933, **2**, 160; *Brit. Chem. Abs.* **B**, 1934, 915.

[154] L. A. Peletier, *Proc. World Petroleum Congr.*, *London*, 1933, **2**, 161, *J. Inst. Pet. Tech.*, 1934, **20**, 75A; *Brit. Chem. Abs.* **B**, 1934, 1046.

[155] D. R. Pye, *Proc. World Petroleum Congr.*, *London*, 1933, **2**, 186; *Brit. Chem. Abs.* **B**, 1934, 1046; *J. Inst. Pet. Tech.*, 1934, **20**, 235A.

[156] C. Bonnier and H. Moynot, *Compt. rend.*, 1933, **197**, 1388; *Brit. Chem. Abs.* **B**, 1934, 354.

[157] C. Bonnier and H. Moynot, *Ann. combust. liquides*, 1934, **9**, 481; *J. Inst. Pet. Tech.*, 1934, **20**, 505A; *Chem. Abs.*, 1934, **28**, 6291.

[158] G. G. Brown and C. A. Marshall, *Nat. Pet. News*, 1934, **26** (20), 29; *J. Inst. Pet. Tech.*, 1934, **20**, 408A.

[159] E. Endo and H. Furuya, *J. Fuel Soc. Japan*, 1935, **14**, 35; *Brit. Chem. Abs.* **B**, 1935, 614.

[160] G. Edgar, *S.A.E. Journal*, 1931, **26**, 452.

[161] D. B. Brooks, N. R. White and G. C. Rodgers, *S.A.E. Journal*, 1931, **26**, 445. See also H. F. Huff, *Oil, Gas J.*, 1934, **32** (40), 20, 43; *J. Inst. Pet. Tech.*, 1934, **20**, 236A.

[162] J. M. Campbell, W. G. Lovell and T. A. Boyd, *S.A.E. Journal*, 1931, **26**, 459.

[163] H. F. Huff, J. R. Sabina and J. B. Hill, *S.A.E. Journal*, 1931, **26**, 464

[164] R. Heinze and M. Marder, *Angew. Chem.*, 1935, **48**, 335, 776; *Chem. Abs.*, 1935, **29**, 5641; *Brit. Chem. Abs.* **B**, 1935, 660. See Chapter 50.

THE EFFECT OF TETRAETHYL LEAD ON KNOCK RATINGS

Hebl, Rendel and Garton[166] brought out the fact that, in addition to its antiknock value, every gasoline has a property which may be defined as its "lead susceptibility" and which determines the amount of increase in antiknock value for any given concentration of tetraethyl lead. A special chart was devised, called an "Ethyl Blending Chart," into which were embodied the factors which determine the octane number of an ethylized gasoline in their proper relation. It was found that by use of this chart,[167] shown in Fig. 249, the reliability of estimated octane numbers of ethylized gasolines could be considerably improved, and also the lead susceptibility of the base gasoline could be conveniently determined. The five factors which determine the octane number of any ethylized gasoline are:

1. The effectiveness of isooctane at different concentrations in raising the antiknock value of isooctane-heptane mixtures, i.e., the relative "dimensions" of octane numbers in different parts of the scale.
2. The effectiveness of tetraethyl lead at different concentrations. This compound is more effective in small concentrations and, as more is added to a gasoline, its effect gradually diminishes.
3. The octane number of the base gasoline before tetraethyl lead is added.
4. The "lead susceptibility" of the gasoline.
5. The number of cubic centimeters of tetraethyl lead added per gallon of gasoline, called the "lead requirement" of the fuel.

In using the chart shown in Fig. 249 the lead susceptibility of any of the gasolines plotted can be determined by extending a line from the star on the left-hand side of the chart through to the lead susceptibility scale on the right-hand side so that the line is parallel to the line already plotted for the gasoline in question. It was believed that the lead susceptibility of a gasoline is not dependent on the hydrocarbons alone but may be markedly affected by impurities e.g., disulphides and other sulphur compounds. The reduction of lead susceptibility has been studied by Schulze and Buell,[168] who report that the disulphides, except carbon disulphide, have the most harmful, the thioethers less and thiocyclic compounds the least harmful, effect on lead response. Comparisons between some aliphatic sulphides and between some aliphatic disulphides show that the reduction of octane number is greater with homologues of higher molecular weight and with branched chain isomers. Considerable lowering of octane number was also noted when aromatic disulphides were present and the concentraton of tetraethyl lead low.

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[165] M. Marder, *Oel u Kohle*, 1935, 11, 923; *Brit. Chem. Abs.* **B**, 1936, 83; *J. Inst. Pet. Tech.*, 1936, **22**, 145A. See also T. Suwa, *Imp. Fuel Research Inst. Japan*, 1935, **30**; *Chem. Abs.*, 1935, **29**, 5641.

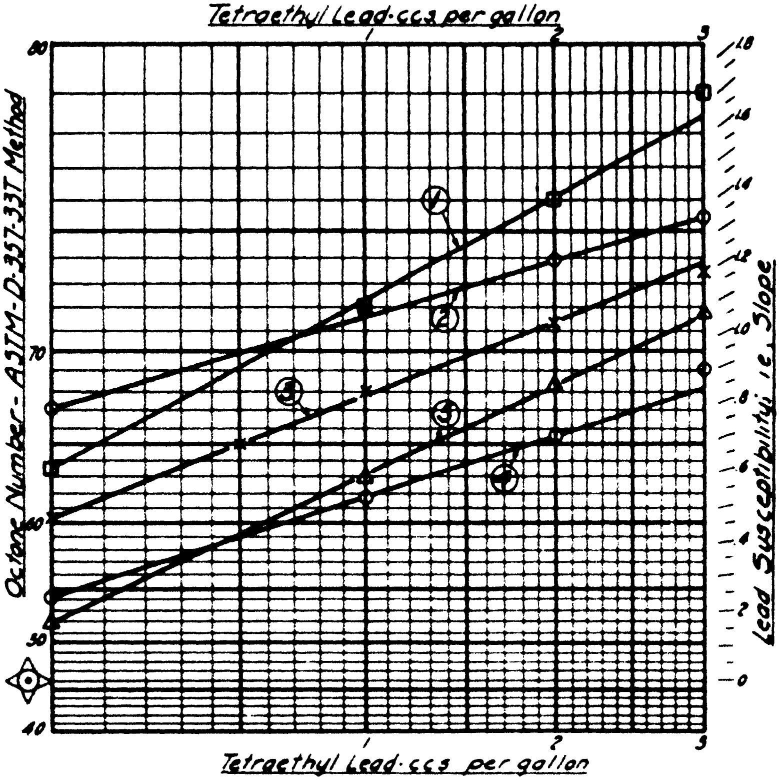
[165a] Use of density at 15°C. has been proposed also. M. Marder, *Oel u. Kohle*, 1936, **12**, 1061, 1087; *J. Inst. Pet. Tech.*, 1937, **23**, 67A

[166] L. E. Hebl, T. B. Rendel and F. L. Garton, *Ind. Eng. Chem.*, 1933, **25**, 187; *Chem. Abs.*, 1933, **27**, 1493; *Brit. Chem. Abs.* **B**, 1933, 293.

[167] The chart pictured in Fig. 249 was furnished by L. E. Hebl (private communication). It differs from the one used by Hebl, Rendel and Garton (*loc. cit.*) in that it is based on data obtained by the A.S.T.M. method D357-36T rather than by the C.F.R. method.

[168] W. A. Schulze and A. E. Buell, *Nat. Pet. News*, 1935, **27** (41), 25; *Oil, Gas J.*, 1935, **34** (21), 22; *Chem. Abs.*, 1935, **29**, 8306. See also Chapter 19.

Investigations by Tongberg[169] and co-workers on the susceptibility of several gasolines (or fractions of these) to tetraethyl lead and aniline revealed that octane number and lead suspectibility are not dependent alone on the boiling range of the fuel. Fractions of the same boiling range (prepared from various gasolines) had



Courtesy Shell Petroleum Corp

FIG. 249.—Ethyl Blending Chart for Several Gasolines. (L. F. Hebl, T. B. Rendel and F. L. Garton)

(Data obtained with C.F.R. engine using A.S.T.M. method D357-36T)

1. Stabilized natural gasoline
2. Cracked gasoline
3. Cracked gasoline (50 per cent) + West Texas straight-run gasoline (50 per cent)
4. West Texas straight-run gasoline
5. Mid-Continent straight-run gasoline

considerably different octane numbers and lead susceptibilities. This was attributed to different types of hydrocarbons and sulphur compounds being present which boil in the same ranges. It is the opinion of Tongberg and co-workers that the effect of hydrocarbon structure in these fractions should not be overlooked. The addition of aniline up to 7 (volume) per cent gave a practically linear increase in octane number for straight-run gasolines, whereas tetraethyl lead gave only small increases in octane number when over 2 to 3 cc. per gallon were used. In cracked gasoline, aniline gave a greater increase in octane number for the first 2 per cent than it did for the second 2 per cent, but from 2 to 7 per cent the increase in octane number was again linear. This property of aniline suggested the possibility that it might supplement the action of tetraethyl lead by acting independently. Certain cracked gasolines were easily brought up to 80 octane number or higher by the use of aniline and tetraethyl lead together, whereas the use of tetraethyl lead alone failed to accomplish this result.

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[169] C. O. Tongberg, D. Quiggle, E. M. Foy and M. R. Fenske, *Ind. Eng. Chem.*, 1936, **28**, 792; *J. Inst. Pet. Tech.*, 1936, **22**, 355A; *Chem. Abs.*, 1936, **30**, 6177. See also W. T. Ziegenhain, *Oil, Gas J.*, 1934, **33** (32), 51 for a discussion of a curve that may be used to determine the amount of lead that must be added to give a desired octane number to a gasoline.

Reports from other investigators[170] revealed that the reason for all the effects being smaller for cracked than for straight-run gasoline is inherent in the hydrocarbon constituents of the gasoline and not due to sulphur compounds or other impurities. Brown and Singer[171] found that cracked gasolines were superior to leaded gasolines of the same octane number.

Effect of Type of Gasoline on Knock Rating

Tongberg and co-workers[172] suggest that the three possible ways of obtaining a motor fuel of higher antiknock value from Pennsylvania gasoline are as follows: the fractions of high antiknock value could be segregated, the fractions of high antiknock value and high blending value could be blended with fractions of only moderate antiknock value to give greater volume of fuel, and the fractions of best octane number could be blended with those most responsive to tetraethyl lead.

Trimble[173] in comparing the antiknock characteristics of vapor-recovery and natural gasoline blends, found that the octane ratings for the former were higher than those of equivalent natural gasoline blends regardless of the method of test. However, natural gasoline was found to be appreciably more lead responsive than vapor recovery gasoline. It was also observed[174] that the antiknock properties of certain gasolines could be increased by cracking the latter at a temperature of 450°C. and at a pressure from 40 to 110 atmospheres.

The separation of knock inducing constituents from motor fuels has been carried out by Voorhees.[175] This method involves distilling the motor fuel into narrow boiling fractions which are refrigerated to give liquid and solid constituents, the latter being rejected.

Detonation in the Diesel Type Engine

Investigations on the ignition quality of Diesel fuels showed that it was advantageous to base all ignition data on reference fuels, for which on theoretical considerations, cetene, $C_{16}H_{32}$, and mesitylene, C_9H_{12}, were suggested, since the former substance will ignite readily in a Diesel engine while the latter does not.[176] The routine rating of fuels is made by measuring the difference in delay of ignition at two pressures, 15 and 30 atmospheres, and expressing the result in terms of reference fuels so as to give each fuel a "cetene number," this being the percentage of cetene in the standard fuel blend which matches the sample tested.[176a] Ignition in this type of engine is said to depend principally upon the chemical structure of the fuel, and the air temperature and pressure, whereas combustion is dependent on correct mixture strength and turbulence. Knock is caused by delay during ignition and is the effect of a too rapid change in pressure rise. In a weakly constructed engine a too-rapid pressure rise will cause what is known as rough running.[177]

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[170] R. Kobayashi, M. Furihata and S. Kajimoto, *J. Soc. Chem. Ind. Japan*, 1935, **38**, 654; *Brit. Chem. Abs.* **B**, 1936, 179, *Chem. Abs.*, 1936, **30**, 2737.

[171] G. G. Brown and S. C. Singer, *Nat. Pet. News*, 1934, **26** (23), 21; *Oil Gas J.*, 1934, **33** (10), 80, 96; *Brit. Chem. Abs.* **B**, 1935, 212; *Chem. Abs.*, 1934, **28**, 6990.

[172] C. O. Tongberg, D. Quiggle and M. R. Fenske, *Ind. Eng. Chem.*, 1936, **28**, 201; *Chem. Abs.*, 1936, **30**, 2736; *Brit. Chem. Abs.* **B**, 1936, 307.

[173] H. N. Trimble, *Proc. 12th Ann. Conv. Nat. Gasoline Assoc.*, **1933**, 32; *Oil Gas J.*, 1933, **31** (52), 58, 60; *J. Inst. Pet. Tech.*, 1934, **20**, 312 A; *Chem. Abs.*, 1933, **27**, 4660.

[174] A. L. Feigin and V. A. Butkov, *Neft. Khoz.*, 1933, **25** (10), 45; *Brit. Chem. Abs.* **B**, 1934, 867; *Chem. Abs.*, 1934, **28**, 3571. See also N. Williams, *Oil Gas J.*, 1934, **33** (9), 11, *J. Inst. Pet. Tech.*, 1934, **20**, 611A; *Chem. Abs.*, 1934, **28**, 6990.

[175] V. Voorhees, U. S. P. 1,951,780, March 20, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1934, **28**, 3579; *J. Inst. Pet. Tech.*, 1934, **20**, 376A.

[176] G. D. Boerlage and J. J. Broeze, *J. Soc. Automotive Eng.*, 1932, **31** (1), 283. See also T. B. Hetzel and P. H. Schweitzer, *ibid.*, 1936, **38**, 206; *Chem. Abs.*, 1936, **30**, 5774.

BLENDED MOTOR FUELS

From time to time various blends of gasoline with other materials, e.g., ethanol, methanol, benzene, or ketones, as well as the use of other liquid or even gaseous fuels have been proposed to replace gasoline in the spark-ignited internal combustion engine. Also a few such blends have been suggested for the Diesel type of engine. Reasons for this development are various, the principal ones being of an economic nature, as for example, fear of a gasoline shortage, the substantially higher cost of this fuel in non-petroleum producing countries, and the utilization of fuel sources within individual nations to make them less dependent on outside sources. A more important but apparently less contributing factor in developing fuel blends has been the desire to improve fuels from various standpoints.[178]

Alcohol Blends. Much attention has been devoted to the employment of alcohols, particularly ethanol, in gasoline blends. In many of the European countries laws have been passed requiring the use of alcohol-gasoline blends as motor fuels mainly as a proposal to benefit agricultural interests.[179] Mixtures containing up to 25 or 30 per cent alcohol have been advocated in order to consume the surplus.[180] Also, in the United States some effort has been made to utilize fuels of this type.[181] The assumptions on which this proposal was made are summarized by Egloff and Morrell[182] as follows: (a) alcohol-gasoline is a superior motor fuel, (b) it is more economical than gasoline, (c) there is an impending shortage of crude oil[183] which would be conserved by use of alcohol, (d) European experience upholds the practicability of the plan, and (e) use of such blends will solve the economic problems of agriculture to some extent. Many investigators, including Egloff and Morrell, point out that some of these assumptions are erroneous.

[176a] "Cetane number" has also been used to determine the ignition quality of Diesel fuels. This is defined (A. L. Foster, *Nat. Pet. News*, 1936, **28** (4), 19) as the numerical value of the percentage of cetane in a blend with methylnaphthalene which shows the same ignition quality as that of a given fuel tested. See also P. H. Schweitzer and T. B Hetzel, *Oil Gas J.*, 1936, **34** (36), 36; *J. Inst. Pet. Tech.*, 1936, **22**, 161A; *Chem. Abs.*, 1936, **30**, 2739. F. H. Garner, *J. Inst. Pet Tech*, 1936, **22**, 503, 460A; *Chem. Abs.*, 1936, **30**, 7317

[177] See also G. D. Boerlage and J. J. Broeze, *Proc. World Petroleum Congr., London*, 1933, **2**, 271; *Brit. Chem. Abs.* **B**, 1934, 1046. R. Stansfield, *J Inst Pet. Tech*, 1934, **20**, 418, *Chem Abs.*, 1934, **28**, 4581; *Brit. Chem. Abs.* **B**, 1934, 949

[178] For an extended discussion of various types of motor fuels see A. W Nash and D A Howes, "The Principles of Motor Fuel Preparation and Application," Chapman and Hall, Ltd., London, 1934. Also, Carleton Ellis and J. V. Meigs, "Gasoline and Other Motor Fuels," D Van Nostrand Co., New York, 1921. E. H. Leslie, "Motor Fuels," The Chemical Catalog Co., Inc, New York, 1923. H. Moore, "Liquid Fuels," The Technical Press, Ltd, London, 1935.

[179] See E. B. Evans, *J. Inst. Pet. Tech.*, 1934, **20**, 392; *Chem. Abs.*, 1934, **28**, 4581 I. Doynel, *Bol. Inform. Petroleras (Buenos Aires)*, 1935, **12**, 129; *J. Inst. Pet. Tech.*, 1936, **22**, 151A. A. Corbett, *Petroleum Times*, 1933, **30**, 459; *Chem Abs.*, 1934, **28**, 283. C. Y. Hopkins, *Can. Chem. Met.*, 1934, **18**, 2; *Chem. Abs.*, 1934, **28**, 2155. See also *Chemical Industries*, 1936, **39**, 409; L. A. Helwich, *Ind. Eng. Chem.*, *News Ed.*, 1936, **14** (20), 413; *Chem. Abs.*, 1936, **30**, 6163.

[180] P. Dumanois, *Ind. chim. belge.*, 1934 (2), **5**, 173; *Chem Abs.*, 1934, **28**, 4201. N. Parravano, *Giorn. chim. ind. applicata*, 1931, **13**, 457; *Chem. Abs.*, 1932, **26**, 1413. K. R. Dietrich, *Allgem. Oel-u. Fett-Ztg.*, 1936, **33**, 76; *Chem. Abs.*, 1936, **30**, 3615

[181] See, for example, F. P. Garvan, "Proceedings of Second Dearborn Conference of Agriculture, Industry and Science." The Chemical Foundation, Inc, 1936, p. 85. W W. Buffum, *ibid.*, 108. F. F. Kishline, *ibid.*, 121. B. T. Brooks, *ibid*, 125. F. A. Eldean, *ibid*, 131.

[182] G. Egloff and J. C. Morrell, *Ind. Eng. Chem.*, 1936, **28**, 1080; *Chem. Abs.*, 1936, **30**, 8572; *Brit. Chem. Abs.* **B**, 1936, 1076.

[183] See, in this instance, B. T. Brooks, *Ind. Eng. Chem.*, 1936, **28**, 1477. G. Egloff and J. C. Morrell, *ibid*, 1478.

One of the primary objections to blends of ethanol or methanol with gasoline is that the alcohol tends to separate in the presence of small percentages of water, although, when anhydrous, ethanol is miscible with gasoline over a wide temperature range.[184] However, the water tolerance of ethanol-gasoline mixtures may be increased by the addition of a liquid or solid blending agent. Among these proposed are benzene and toluene,[185] hexahydronaphthalene,[186] acetone, ethyl ether, *n*-butyl alcohol, isoamyl alcohol[187] and isopropyl alcohol.[188] Blenders suggested by Bereslavsky[189] include menthol, geraniol, citronellol, steam-distilled pine oil, terpineol, fenchyl alcohol and borneol, used in the proportions: 5 per cent blender, 85 per cent gasoline, and 10 per cent anhydrous alcohol.

In the case of methanol, there is more difficulty in blending with gasoline unless aromatic hydrocarbons are present. Howes,[190] and Gordon,[191] report extensive studies on the solubility behavior of methanol and the use of blending agents. The solubility of this alcohol in paraffins is rather low whereas in aromatics it is quite high. Hence one of the blending agents suggested is benzol. However, it is stated that the higher aliphatic alcohols are more efficient in this respect.[192] According to Shepherd[193] the addition of 10 to 15 per cent acetone greatly increases the miscibility of methanol and gasoline.

Some of the advantages and disadvantages of ethanol-gasoline blends as motor fuels are pointed out by Egloff and Morrell.[194] Ethanol has a high octane rating and increases the antiknock properties of gasoline to which it is added.[195] Thus, 10 per cent of ethanol raised the octane rating of a 63 octane gasoline to 72 and of a 61 octane rating to 70. At the same time there is an over-all increase in fuel consumption of 5 per cent for every 10 per cent of alcohol added. Even with improvements in engine design to obtain the highest useful compression ratio it was pointed out that because of the lower calorific value of alcohol[196] there would still be an over-all increase in fuel consumption of 2 per cent with a 10 per cent blend, and of 3.8 per cent with 20 per cent of alcohol.[197]

Since ethanol has a higher ignition temperature and a higher latent heat of vaporization than gasoline, Egloff and Morrell state that cold starting will be more difficult.[198] Warm starting would also be interfered with because of the greater volatility of the blends at higher temperatures.[199] This is indicated in the distillation curves for mixtures of gasoline with various percentages of ethanol. See Fig. 250. Another difficulty pointed out for these blends is the effect on vapor lock tendencies. Vapor lock occurs in a fuel system when too much vapor fuel is present in proportion to liquid fuel so that the engine receives an insufficient supply of the latter.[200] It was found that for the temperature range 105° to 135°F. addition of 5 per cent ethanol doubled the ratio of vapor volume to liquid volume as compared with that for gasoline alone. In Table 201 the relationship of alcohol percentage to the temperature at which vapor lock occurs is presented. From this it is seen that 1-10 per cent blends of alcohol result in appreciable lowering of vapor-lock temperature. However, Bridgeman[201] states that this tendency can be overcome if the gasoline used for blending has a lower vapor pressure than that of the gasoline with which the blend is to be compared. Also, it is asserted that

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[184] O. C. Bridgeman and D. Querfeld, *Ind. Eng. Chem.*, 1933, **25**, 523. See also J. Herbrich, *Ann. combust. liquides*, 1933, **8**, 1313; *Chem. Abs.*, 1934, **28**, 1501. W. R. Ormandy, T. W. M. Pond and W. R. Davies, *J. Inst. Pet. Tech.*, 1934, **20**, 308, 913; *Chem. Abs.*, 1934, **28**, 4862; *Brit. Chem. Abs.* **B**, 1934, 530. The latter work also includes data on other aliphatic alcohols.

[185] O. C. Bridgeman, *Ind. Eng. Chem. News Ed.*, 1933, **11**, 139; *Chem. Abs.*, 1933, **27**, 3057.

[186] T. Araki and M. Nakabayashi, *J. Soc. Chem. Ind. Japan*, 1934, **37**, 685B; *Brit. Chem. Abs.* **B**, 1935, 293; *Chem. Abs.*, 1935, **29**, 907.

[187] E. C. Koo, Nai Chen Chien, Yieng Tung Chu and Shiu Ming Cheng, *Ind. Center (China)*, 1934, **3**, 112; *Chem. Abs.*, 1936, **30**, 2725. E. C. Koo, *Ind. Research (China)*, 1936, **5**, 161; *Chem. Abs.*, 1936, **30**, 7815.

[188] C. H. Bayley and C. Y. Hopkins, *Can. J. Research*, 1934, **11**, 505; *Chem. Abs.*, 1935, **29**, 401; *Brit. Chem. Abs.* **B**, 1935, 86. According to these workers, if half the ethanol in a given blend is replaced by isopropanol the critical water content at -20°C is increased by 60 per cent. For a study of engine performance and fuel consumption of gasoline-ethanol and isopropanol blends see M. S. Kuhring, *Can. J. Research*, 1934, **11**, 489; *Chem. Abs.*, 1935, **29**, 337; *Brit. Chem. Abs.* **B**, 1935, 86; *J. Inst. Pet. Tech.*, 1934, **20**, 623A.

[189] E. V. Bereslavsky, British P. 444,026, 1936; *Chem. Abs.*, 1936, **30**, 6537; *Brit. Chem. Abs.* **B**, 1936, 584; *J. Inst. Pet. Tech.*, 1936, **22**, 266A.

[190] D. A. Howes, *J. Inst. Pet. Tech.*, 1933, **19**, 301.

[191] K. Gordon, *Proc. World Petr. Cong.*, London, 1933, **2**, 788; *Chem. Abs.*, 1934, **28**, 3866; *Brit. Chem. Abs.* **B**, 1934, 788.

[192] See also T. Hammerich, *Oel u. Kohle*, 1936, **12**, 641; K. R. Dietrich and W. Lohrengel, *ibid.*, 455; *J. Inst. Pet. Tech.*, 1936, **22**, 403A; *Chem. Abs.*, 1936, **30**, 8572.

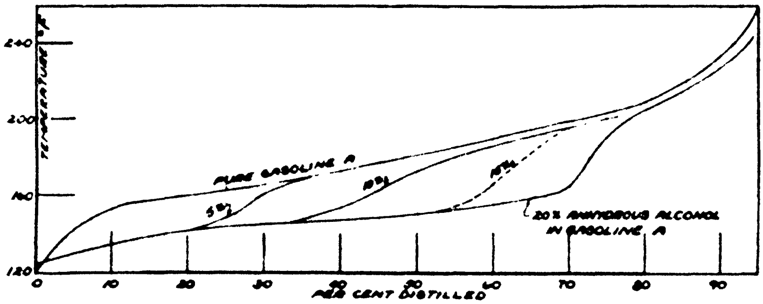
[193] F. M. F. Shepherd, *J. Inst. Pet. Tech.*, 1934, **20**, 294; *Chem. Abs.*, 1934, **28**, 4862; *Brit. Chem. Abs.* **B**, 1934, 531.

[194] G. Egloff and J. C. Morrell, *Ind. Eng. Chem.*, 1936, **28**, 1080; *Chem. Abs.*, 1936, **30**, 8572; *J. Inst. Pet. Tech.*, 1936, **22**, 506A. See also J. C. Morrell, *Agr. Eng.*, 1933, **14**, 220; *Chem. Abs.*, 1934, **28**, 875. A. L. Foster, *Nat. Pet. News*, 1936, **28** (17), 20. J. C. Vlugter, *Chem. Weekblad*, 1933, **30**, 570; *Chem. Abs.*, 1933, **27**, 5525.

[195] See also, A. L. Teodoro, *Philippine Agr.*, 1935, **24**, 352; 1936, **24**, 839; *Chem. Abs.*, 1936, **30**, 265, 1964. J. G. Bechtle, *Sugar News*, 1934, **15**, 262; *Chem. Abs.*, 1934, **28**, 4861. U. Mohr, *Oel u. Kohle*, 1936, **12**, 713; *Brit. Chem. Abs.* **B**, 1936, 967; *Chem. Abs.*, 1936, **30**, 8571.

[196] See J. C. Lichty and E. J. Ziurys, *Ind. Eng. Chem.*, 1936, **28**, 1094; *J. Inst. Pet. Tech.*, 1936, **22**, 505A; *Chem. Abs.*, 1936, **30**, 8572; *Brit. Chem. Abs.* **B**, 1936, 1076.

[197] See also S. Saijo, *J. Fuel Soc. Japan*, 1935, **14**, 133; *Chem. Abs.*, 1936, **30**, 6531; *J. Inst. Pet. Tech.*, 1936, **22**, 154A; *Brit. Chem. Abs.* **B**, 1936, 178.



Courtesy Industrial and Engineering Chemistry

FIG. 250.—Effect of Ethyl Alcohol on Gasoline Distillation Curve. (G. Egloff and J. C. Morrell)

TABLE 201.—*Effect of Alcohol on Vapor Lock Tendency in Gasoline-Ethanol Blends.*

Composition of Fuel		Temp. of Vapor Lock	Composition of Fuel		Temp. of Vapor Lock
% Alcohol	% Gasoline	°F.	% Alcohol	% Gasoline	°F.
0	100	118	5	95	111
1	99	113	10	90	112
2	98	110	20	80	114
3	97	110	30	70	116
4	96	111	40	60	118

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[198] On the other hand it has been stated that the flash point of a gasoline is raised from −38°C. to −30°C. on addition of 20 per cent ethanol and that starting in cold weather can be aided by preheating the air supplied to the engine. See G. Roberti, *Energica termica*, 1934, **2**, 211; *Chimie et industrie*, 1934, **33**, 352; *Chem. Abs.*, 1935, **29**, 1133.

[199] See, however, O. Wawrzinoik, *Automobiltech. Z.*, 1933, **36**, 464, 496, *Chem. Abs.*, 1934, **28**, 1501, who states that the type of fuel has but little influence on the starting characteristics of an engine.

[200] For data on the total and partial vapor pressures of mixtures of ethanol with various gasoline hydrocarbons see, Y. Nagai and N. Ishii, *Proc. Imp. Acad. (Tokyo)*, 1935, **11**, 23, *J. Soc. Chem. Ind. Japan*, 1935, **38**, Suppl. binding, 86; *Chem. Abs.*, 1935, **29**, 3491, 3805. Also N. Ishii, *J. Soc. Chem. Ind. Japan*, 1935, **38**, Suppl. binding, 659, 705, *Chem. Abs.*, 1936, **30**, 2725, 3199; *Brit. Chem. Abs.* **B**, 1936, 356.

[201] O. C. Bridgeman, *Ind. Eng. Chem.*, 1936, **28**, 1102; *Chem. Abs.*, 1936, **30**, 8572, *J. Inst. Pet. Tech.*, 1936, **22**, 507A; *Brit. Chem. Abs.* **B**, 1936, 1076.

freedom from vapor lock can be obtained by proper design of fuel lines to handle alcohol blends.

Other disadvantages reported are that there is likely to be corrosion of containers and fuel systems unless the blends are kept absolutely water-free,[202] and that under conditions where the alcohol undergoes only partial combustion, organic acids are formed which will cause corrosion of cylinders and exhaust manifolds, especially if condensation of moisture occurs in the presence of combustion products. Such conditions would be promoted by low temperatures and intermittent operation of the engine.[203] Also it was pointed out that ethanol-gasoline blends cause overheating (of motors) which, however, has one advantage in that carbon formation decreases. On the other hand, lubrication is likely to be impaired because of an increased tendency to burn the lubricating oil film from the cylinder walls. One suggested method for overcoming this is to add lubricating oil to the fuel. Another is to incorporate 0.5 per cent of oleic acid in the lubricating oil.[204]

In summarizing the reports of various investigations of alcohol-gasoline blends, Christensen[205] concludes that properly prepared fuels of this type containing up to 25 per cent alcohol may be used interchangeably with gasoline of equal antiknock rating. Also he considered that the slight difference in fuel consumption was not of great importance and stated that the various reports of abnormal corrosion by alcohol fuels have been traced to use of corrosive denaturants. Winter operation was said to be particularly pleasing because of the elimination (by alcohol) of ice-formation in the fuel system.[206]

Bridgeman,[207] in analyzing the differences between alcohol blends and gasoline itself, stated that for a fair comparison of performance a common basis must be established since the properties of fuels vary with the conditions of testing. If no adjustment is made in carburetor or spark settings when comparing the two types of fuel some cars will show more fuel consumption and some less with a 10 per cent alcohol blend than with gasoline alone for the same power output. This is attributed to the fact that the blends require a smaller air-to-fuel ratio than gasoline for maximum power[208] and that on the average, carburetor settings are distributed equally on each side of the 12:1 ratio for gasoline. With 20 and 40 per cent blends, however, the tendency would be for higher fuel consumption. On the other hand, if the spark and carburetor settings are varied to suit the individual fuel, there will be an increase of 3 to 4 per cent in fuel consumption with a 10 per cent blend and about double this amount with a 20 per cent blend. Also, if advantage is taken of the higher compression ratio, a properly designed engine will give better power and acceleration with an alcohol blend than with gasoline alone. However, it was also stated that no matter what gain in performance can be obtained by better engine design with alcohol blends, still better performance per gallon will be secured with gasoline of higher octane number in the same engine.[209]

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[202] See K. R. Dietrich, *Chem. Ztg.*, 1934, **58**, 519; *J. Inst. Pet. Tech.*, 1934, **20**, 468A. K. R. Dietrich and W. Lohrengel, *Oel u. Kohle*, 1936, **12**, 91; *J. Inst. Pet. Tech.*, 1936, **22**, 154A. M. Louis, *Chimie et industrie*, 1929, *Feb. Special No.*, 312; *Chem. Abs.* 1929, **23**, 3789.

[203] The composition of exhaust gases from gasoline-alcohol mixtures is discussed by J. Formanek, *Automobiltech. Z.*, 1934, **37**, 234; *Chem. Abs.*, 1935, **29**, 909. See also J. Formanek and J. Dvorak, *Chem. Obzor*, 1933, **8**, 107, 129; *Chem. Abs.*, 1933, **27**, 5170.

[204] H. Miller, *Agr. Eng.*, 1933, **14**, 274; *Chem. Abs.*, 1934, **28**, 3555.

[205] L. M. Christensen, *Ind. Eng. Chem.*, 1936, **28**, 1089; *Chem. Abs.*, 1936, **30**, 8572; *Brit. Chem. Abs.* **B**, 1936, 1076; *J. Inst. Pet. Tech.*, 1936, **22**, 506A. See also T. Suiva, *J. Fuel Soc. Japan*, 1935, **14**, 129; *J. Inst. Pet. Tech.*, 1936, **22**, 154A; *Brit. Chem. Abs.* **B**, 1936, 178. R. B. Gray; *Agr. Eng.*, 1933, **14**, 185; 1934, **15**, 106; *Chem. Abs.*, 1934, **28**, 2495, 5956. W. Gay, *Wisconsin Engr.*, 1935, **40**, 3, 18; *Chem. Abs.*, 1936, **30**, 4297.

[206] See also A. Swan, *Aircraft Engineering*, 1936, **8** (83), 3; *J. Inst. Pet. Tech.*, 1936, **22**, 110A. A. A. Griffith and W. Helmore, British P 414,410, 1934; *Chem. Abs.*, 1935, **29**, 595.

[207] O. C. Bridgeman, *Ind. Eng. Chem.*, 1936, **28**, 1102; *Chem. Abs.*, 1936, **30**, 8572; *Brit. Chem. Abs.* **B**, 1936, 1076; *J. Inst. Pet. Tech.*, 1936, **22**, 507A.

[208] See L. T. Brown and L. M. Christensen, *Ind. Eng. Chem.*, 1936, **28**, 650; *Chem. Abs.*, 1936, **30**, 5401; *J. Inst. Pet. Tech.*, 1936, **22**, 354A; *Brit. Chem. Abs.* **B**, 1936, 775.

Benzene Blends. In some instances alcohol blends contain considerable percentages of benzene or commercial benzol. Proponents of this type of fuel state that it is superior in many respects to a simple alcohol-gasoline blend or to a benzol-gasoline blend.[210] Representative proportions are gasoline 50-65 per cent, benzene 20-40 per cent and alcohol 10-20 per cent.[211] It has been pointed out that because of the high melting point of benzene (5.5°C.) the proportions of components in this type of blend are limited somewhat by the temperatures at which the fuel is to be used.[212] The water tolerance of such fuels is said to increase with the percentage of alcohol[213] but as in the case of the alcohol-gasoline mixtures blending agents are found to be helpful. For example, the presence of 0.9 per cent of pyridine oleate is said to permit the tolerance of 0.5 part of water in a mixture of 18 parts methanol, 18 parts benzene and 54 parts of gasoline.[214] An investigation of various homogenizers for a blend of 40 per cent alcohol, 40 per cent gasoline and 20 per cent benzene has been made by Grossman.[215] α-Naphthol was found to be most effective with β-naphthol and ethyl ether somewhat less so. Other substances tried were benzene, naphthalene and a middle oil from gas coal tar. The effect of the agents is shown in Table 202.

TABLE 202.—*Homogenizing Agents for Mixed Fuels.*

	Fuel Alone	5% Naphthalene	5% Benzol	10% Benzol	5% Middle Oil	10% Middle Oil	5% Ether	10% Ether	5% β-Naphthol	5% α-Naphthol
Temp. of Separation °C.	−6	−11	−11	−16	−14	−23	−23	−44	−22	−28
Percentage of Water Added to Cause Separation at 18°C.	0.9	1.1	1.0	1.2	1.3	1.7	1.6	2.2	2.1	2.2

Comp. of Fuel: 95% Alcohol—40%; Gasoline—40%; Benzene—20%

Other Blends. Mixtures of benzene, or more usually of crude benzol, containing benzene and some of its homologues, with gasoline are employed to some extent as motor fuels.[216] Other organic liquids suggested for admixture with gasoline to improve its characteristics from various standpoints include ethyl ether, acetone[217] and ethyl peroxide.[218] It is reported that isopropyl ether is as good as isooctane for blending with gasoline to improve octane rating.[219] A 74-octane gasoline was raised to 100 octane value by blending with 40 per cent isopropyl ether and 3 cc. of lead tetraethyl per gallon.

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[209] Polymer gasoline is one source of such fuel. See G. Egloff, *Ind. Eng. Chem.*, 1936, **28**, 1461; *Chem. Abs.*, 1937, **31**, 1189. See also Chapter 26

[210] See, e.g., J. Formanek, *Chem. Obzor*, 1934, **9**, 1, 27; *Automobiltech Z.*, 1935, **38**, 409; *Chem. Abs.*, 1934, **28**, 4861; 1936, **30**, 3201. C. Conrad, *Brennstoff-Chem.*, 1934, **15**, 181; *Brit. Chem. Abs.* **B**, 1934, 662. K. R. Dietrich, *Automobiltech. Z.*, 1933, **36**, 519; *Chem. Abs.*, 1934, **28**, 1165.

[211] R. Fritzweiler and K. R. Dietrich, *Proc. World Petroleum Congr.*, *London*, 1933, **2**, 784; *Chem. Abs.*, 1934, **28**, 3866. J. Verdier, *Chimie et industrie*, 1934, **31**, (*April Special No.*), 364; *Chem. Abs.*, 1934, **28**, 5625; *Brit. Chem. Abs.* **B**, 1934, 662. P. Dumanois, *Bull. assoc. sucr. dist.*, 1932, **50**, 329; *Chem. Abs.*, 1933, **27**, 5170.

[212] For freezing point determinations of various gasoline, benzene and alcohol mixtures see L. G. Sabrou and M. Renaudie, *Chimie et industrie*, 1934, **32**, 21; *J. usines gaz.*, 1934, **58**, 122, 148, 208; *Chem. Abs.*, 1934, **28**, 5956, 6549.

[213] H. A. J. Pieters and H. Koopmans, *Chem. Weekblad*, 1933, **30**, 328; *Chem. Abs.*, 1933, **27**, 3380.

[214] M. Chaffette, French P. 755,445, 1933; *Chem. Abs.*, 1934, **28**, 1509.

[215] F. Grossman, *Przemysl Chem.*, 1935, **19**, 245; *Chem. Abs.*, 1936, **30**, 5389

[216] See W. H. Coleman, *Proc. World Petroleum Congr.*, *London*, 1933, **2**, 751; *Petroleum World* (*London*), 1933, **30**, 270; *Chem. Abs.*, 1934, **28**, 3865. L. F. Magness, U. S. P. 1,954,939, April 17, 1934; *Chem. Abs.*, 1934, **28**, 3874; *Brit. Chem. Abs.* **B**, 1935, 216.

Livraghi[220] produced a fuel, said to have high antiknock value, by mixing 40 to 60 per cent by weight of methanol or ethanol with 60 to 40 per cent of light oils or crude benzol from coal or oil shale, adding 2 per cent of naphthalene and subjecting the mixture to thermal cracking at 350-500°C. Other fuels containing alcohol include alcohol, ether and kerosene,[221] alcohol, benzene and 10 per cent water,[222] alcohol (94 per cent), water (5 per cent), gasoline (0.5 per cent) and aniline (0.5 per cent),[223] and alcohol (6) nitrobenzene (3) amyl acetate (1) and a petroleum fraction (10 parts).[224] A mixture of 90 per cent alcohol and 10 per cent acetone saturated with acetylene has also been recommended.[225] A fuel said to contain triethylmethane and trimethylmethane may be made by passing a mixture of vapors of acetyl chloride and ethanol at 200-250°C. over an iron-nickel catalyst.[226]

Annaratone[227] proposed as a motor fuel 59 per cent of ethanol and heptane, 15 per cent of toluene, amyl alcohol and *p*-xylene and 25 per cent of methylcyclohexanol, decahydronaphthalene and tetrahydronaphthalene.

Among various solid materials which have been suggested for improving motor fuels (by incorporation of small percentages in the fuel) are included biphenyl, naphthalene[228] camphor[229] menthol, *p*-dichlorobenzene[230] alkylarylketones and polynitro compounds, e.g., 2,4,6,trinitro-1-methyl-3-*ter*-butylbenzene.[231] Also, it has been proposed to add to motor fuel refined liquid decomposition products obtained from the distillation of rubber.[232] According to Greenstreet,[233] kerosene and Diesel fuels are made more completely combustible by incorporating an oxidizing agent, e.g., a nitrate or peroxide, together with a stabilizing agent such as an amido compound.

Of interest in the consideration of motor fuels are the various proposals to utilize gaseous materials either carried as such in compressed or dissolved form[234] or generated in an apparatus attached to the vehicle.[235] Thus, a mixture 20 to 30 per cent ethane and ethylene, 30 to 40 per cent propene and butene and 30 per cent propane, butane and pentane separated from coke-oven or cracking gases is suggested.[236] Hydrogen, used either alone[237] or in conjunction with liquid hydrocarbon fuels, has also been proposed.[238] Acetylene dissolved in furfural and acetone is advocated by Classen.[239]

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[217] E. G. E. Meyer, British P. 369,731, 1931 and 411,904, 1934, to Brittol Syndicate, Ltd.; *Chem Abs.*, 1933, **27**, 2283; 1935, **29**, 579; *Brit. Chem Abs.* **B**, 1934, 749; *J. Inst. Pet Tech.*, 1934, **20**, 459A. See also *Chem. Age (London)*, 1924, **10**, 156.

[218] R. A. Coustal and H. Spindler, French P 775,851, 1935; *Chem. Abs.*, 1935, **29**, 3141

[219] H. F. Buc and E. E. Aldrin, *S.A.E. Journal*, 1936, **39**, 333, 357T; *Chem Abs.*, 1936, **30**, 7828; *Nat Pet News*, 1936, **28** (25), 25; *Chem. Abs.*, 1936, **30**, 6177. H. E. Buc, U. S. P 2,046,243, June 30, 1936, to Standard Oil Development Co., *Chem. Abs.*, 1936, **30**, 5768. See also Chapter 15

[220] E. Livraghi, U. S. P. 2,037,478, April 14, 1936; *Chem Abs.*, 1936, **30**, 4001; *J. Inst. Pet. Tech.*, 1936, **22**, 266A British P 433,410, 1934 to Soc. anon carburanti Italia; *Brit. Chem Abs* **B**, 1935, 937. French P 755,767, 1933 and 781,936, 1935, *Chem. Abs.*, 1934, **28**, 2177; 1935, **29**, 7053 Italian P. 307,368 and 309,243; see S. Doldi, *Giorn. chim. ind applicata*, 1933, **15**, 593; *Chem Abs.*, 1934, **28**, 2871; *Brit Chem. Abs.* **B**, 1934, 308; *J. Inst. Pet. Tech.*, 1934, **20**, 340A.

[221] R. Avice, *Sugar J.*, 1934, **36**, 347; *Chem Abs.*, 1934, **28**, 6973 See also F. Spausta, *Petroleum Z.*, 1934, **30** (50), 1; *Brit Chem Abs.* **B**, 1935, 133; *Chem Abs.*, 1935, **29**, 4229. For a comparison of kerosene and alcohol as fuels see A. B. Calamboy and N. L. Cuevas, *Philippine Agriculturist*, 1935, **24**, 549; *World Petroleum*, 1936, **7**, 210.

[222] A. P. A. Coreth zu Coredo, French P. 760,323, 1934; *Chem. Abs.*, 1934, **28**, 3562

[223] A. I. Teodoro and J. P. Mamisao, *Philippine Agr.*, 1934, **22**, 720; *Chem Abs.*, 1934, **28**, 4201

[224] Y. Shimomura, Z. Takagi and E. Tawara, Japanese P 101,954, 1933; *Chem. Abs.*, 1934, **28**, 5968.

[225] J. Araux, *Anales univ. central Ecuador*, 1933, **50**, 179; *Chem Zentr.*, 1933, **2**, 642; *Chem. Abs.*, 1934, **28**, 5955.

[226] French P. 753,890, 1933 to Fabrication francaise de prod. de lait; *Chem. Abs.*, 1934, **28**, 1168.

[227] D. Annaratone, German P 587,775, 1933; *Chem. Abs.*, 1934, **28**, 1842.

[228] A. Körting, Austrian P. 138,202, 1934; *Chem. Abs.*, 1934, **28**, 6553

[229] S. Bettini, French P. 764,157, 1934; *Chem. Abs* 1934, **28**, 5639. M. B. Mitchell and L. Bentley, British P. 417,946, 1933; *Brit Chem. Abs* **B**, 1935, 11

[230] M. Gross, Austrian P. 143,882, 1935; *Chem Abs.*, 1936, **30**, 2747.

[231] M. Bollmann, German P. 596,535 and 596,536, 1934 to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 5215.

[232] A. P. Sirejols, French P 750,375, 1933; *Chem Abs.*, 1934, **28**, 882.

[233] C. J. Greenstreet, U. S. P. 1,800,997, April 14, 1931; *Chem. Abs.*, 1931, **25**, 3466; *Brit. Chem. Abs.* **B**, 1932, 11.

[234] C. M. Walter, *Proc. World Petroleum Congr., London*, 1933, **2**, 764.

A proposal has been made to utilize such materials as hydrorubber, isobutene polymers, polystyrene and aldol polymers of isobutyraldehyde and diacetone alcohol as sources of motor fuel.[240] The materials are depolymerized with the aid of phosphoric acid or soda lime (as needed) and the products fed to the engine.

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[235] J. Russel, *Proc. World Petroleum Congr., London*, 1933, **2**, 769.

[236] French P. 775,799, 1935, to Ruhrchemie. A.-G.; *Chem. Abs.*, 1935, **29**, 3141.

[237] R. A. Evans and W. H. Campbell, *J. Inst. Fuel*, 1934, **6**, 277; *Chem. Abs.*, 1934, **28**, 7465.

[238] H. C. Gerrish and H. H. Foster, *Nat. Advisory Comm. for Aeronautics Report*, **535**, 1935; *Mech. Engineering*, 1935, **57**, 794; *Automotive Industries*, 1936, **74**, 164.

[239] J. M. H. K. Classen, German P. 616,651, 1935; *Chem. Abs.*, 1935, **29**, 8294.

[240] British P. 408,124, 1934 to I. G. Farbenind. A.-G., *Chem. Abs.*, 1934, **28**, 5968.

Chapter 45

Miscellaneous Oxidation Reactions. Alcohols, Denaturants and Other Products

In a number of the preceding chapters the oxidation of individual hydrocarbons or of certain petroleum fractions has been considered. The products of such reactions are principally ketones, alcohols, esters, aldehydes and various types of aliphatic and aromatic acids and anhydrides. The effect of autoxidation on certain distillates, particularly gasoline and transformer or lubricating oils, has been pointed out. In this chapter are included the production of other compounds, such as alcohols, by oxidation, and the utilization of these petroleum fractions in the preparation of many differing kinds of materials, e.g., denaturants, insecticides, solvents, synthetic resins and waxes, and emulsifying agents. The aliphatic carboxylic acids such as formic acid have been suggested for use in preparation of pickling inhibitors. The organic acid is reacted with sulphurized cinchona bark alkaloid, such as sulphurized quinoidine, and used with dilute sulphuric acid in cleaning metals.[1] Oxidation processes such as that of dehydrogenation are considered. It has been proposed, for instance, that a catalyst capable of dehydrogenating cyclohexane to benzene[2] be made by soaking active carbon in ammonium molybdate, lead nitrate and phosphoric acid and heating (at 300°C.) in a current of sulphur or selenium hydride. The addition reactions involving carbon monoxide constitute another type of oxidation. One instance of this type is the reaction for preparing aliphatic acids by reacting vaporized alcohols and carbon monoxide over a catalyst such as chromic acid on silica gel.[3]

Mild or limited oxidation is sometimes employed in refining processes, particularly when readily polymerized or resinified constituents are to be removed. In some instances sulphur compounds present as impurities may be preferentially oxidized to sulphur dioxide, sulphur and oxides of carbon and thus be removed. A brief review of such methods is included.

OXYGEN AS A POLYMERIZATION CATALYST

The conditions for polymerizing olefins in the absence of a catalyst indicate that a definite pressure-temperature relationship exists, according to Wiezevich and Whiteley.[4] Thus, a pressure of about 2050 pounds per square inch is needed to initiate the polymerization of ethylene in a steel bomb at 345°C. If the temperature is lowered to 335°C., a pressure of 2760 pounds per square inch is required. These conditions they report, are about the minimum for polymerization in the absence of a catalyst, whereas, in order to obtain better rates of reaction, higher pressures or temperatures are needed. The investigators state that for optimum conditions, the polymerization of ethylene without a catalyst should be conducted at 430°C. under 2760 pounds per square inch pressure. Higher pressures or temperatures are required in the polymerization of heavier olefins under like conditions.

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[1] R. E. Lawrence, U. S. P. 2,031,895, Feb. 25, 1936, to Grasselli Chemical Co.; *Chem. Abs.*, 1936, **30**, 2168.

[2] German P. 578,567, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 776.

[3] G. B. Carpenter, Canadian P. 349,270, to Canadian Industries Ltd.; *Chem. Abs.*, 1935, **29**, 4027.

[4] P. J. Wiezevich and J. M. Whiteley, U. S. P. 1,981,819, Nov. 20, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 474; *Brit. Chem. Abs.* B. 1935, 881.

However, the polymerization of such olefins proceeds at much lower temperatures and pressures if a small amount of oxygen is added. The amount of oxygen used may vary within quite wide limits, but the amount employed is generally less than that required to react with the olefins, or to dehydrogenate the unsaturates. The addition of oxygen, they find, is needed only to start the polymerization reaction, which, once started, proceeds rapidly and smoothly at the same relatively mild conditions of temperature and pressure without addition of further oxygen. The optimum conditions of temperature and pressure at which the oxygen should be added depend to some extent on the type of apparatus, the method of treatment, and the olefins used. The exact conditions are best determined by experiment. However, they find that it is generally most satisfactory to add the oxygen to the olefins preheated to a temperature of 200° to 400°C., though other temperatures may be used. The initial pressure to be used (between 10 and 200 atmospheres) depends on the temperature employed. During the reaction, due to polymerization, the pressure may decrease even to atmospheric. According to Wiezevich and Whiteley, with higher molecular weight olefins pressures higher than those needed in the polymerization of ethylene are needed to obtain equivalent yields of liquid products. For example, under the conditions of temperature suitable for polymerization of ethylene at 60 atmospheres pressure, 80 atmospheres are needed for propene and 95 atmospheres for butene. The amount of oxygen added also depends on the operating conditions, large additions tending toward the production of carbon, although the effect of the oxygen disappears entirely at very low concentrations. Ratios of 0.01 to 0.4 mole of oxygen per mole of olefin are the outside limits, beyond which the operation is unsatisfactory. Ratios between 0.03 and 0.2 are most satisfactory. The mole ratio of oxygen required goes in inverse ratio to the molecular weight of the olefin treated. Thus, for ethylene greater mole ratios of oxygen are required than are needed for propene, butene and heavier unsaturates.

The reaction may be conducted in the presence of contact materials such as broken fire brick, silica, alumina or metal wool, which may or may not possess catalytic power *per se* in this type of reaction. The degree of polymerization may be controlled (at given operating conditions) by increase or decrease in contact time. The decrease of pressure observed during the polymerization in batch operation may be used as a rough index of the extent to which the process has proceeded. Long contact (8 to 10 hours) is desirable for more complete reaction, yields of 95 per cent (based on the reacting olefins) being obtained in this way. Shorter contact tends toward the production of lighter liquid products in smaller yields.[5]

Faber[6] has reported that natural gas can be treated with air sufficient only for partial combustion to produce gasoline and fuel gas. The mixture is maintained at a temperature of 500° to 980°C. in a reaction zone by the heat of combustion of the small part oxidized. It is said that no carbon black is formed, but that heavier gasoline hydrocarbons can then be extracted from the residual gas. Oxidation polymerization has been proposed as a method of removing polymerizable material from fuel oils. It has been suggested that this may be accomplished by subjecting the oil vapors to a refluxing action in a dephlegmator tower, while an oxidizing gas such as air is directly added to the tower to accelerate the separation of the polymerized materials.[7]

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[5] For a more complete discussion of polymerization processes, see Chapter 26.

[6] W. F. Faber, U. S. P. 1,961,288, June 5, 1934, to V. N. Roadstrum; *Brit. Chem. Abs.* B, 1935, 295; *J. Inst. Pet. Tech.*, 1934, 20, 500A; *Chem. Abs.*, 1934, 28, 4898.

Oxidation polymerization of asphaltic base oil residues, either those resulting from cracking or non-cracking processes, may be made to yield commercial asphalts. Rose[8] proposes a blend of oily distillate cylinder oil stock, a non-cracking distillation residue free of lubricating oil, and a residue from cracking operations as raw material in this type of oxidation. The blended material is subjected to a mild oxidation, and the asphalt separated from the resulting material. Bray and Beckwith[8a] have produced an asphalt by an oxidation of similar asphaltic residue oils, and report that the separation into oil and bitumen constituents may be made satisfactorily by the use of selective solvents, such as liquid propane. The oil constituent so extracted may be treated with liquid sulphur dioxide to bring about separation into a raffinate and an extract. This second extract is mixed with the bitumen produced in the first step, and further oxidized with air. An asphalt is produced which is characterized by a relatively lower penetration power for the same melting point, and a relatively higher susceptibility to temperature change than the asphalt produced by the primary oxidation. Ragatz[9] reports that the most satisfactory temperature for air oxidation of asphaltic residuum oils to asphalt appears to be about 175°C. The oxidized material is heated to a temperature of about 350°C. to bring about polymerization of the oil fractions present in the asphalt, while sufficient pressure (about 25 pounds per square inch) is maintained to prevent major volatilization of the vaporizable oil fractions.

Légé[10] reports a method of producing either naphthenes, or, carrying the process of dehydrogenation to its limit, coke, by reacting solid, liquid or gaseous hydrocarbons with oxygen in the presence of strong sulphuric acid. Ferric, nickelic or cupric compounds soluble in the sulphuric acid present are added as catalysts. The oils are then blown with steam, or steam and air, under atmospheric pressure. If a temperature of 200° to 250°C. is employed, naphthenes result; if the temperature is raised to 250-300°C., coke is produced.

REFINING BY OXIDATION PROCESSES

According to Herzenberg,[10a] active oxygen attacks sulphur compounds present in petroleum more readily than it does olefinic and unsaturated materials. By this means, he finds, sulphur compounds may be almost entirely eliminated from the petroleum treated. His research was conducted with Mexican Panuco oil containing a total of 5 per cent sulphur as thiophenes, mercaptans, hydrothiophenes and six-membered ring compounds, such as pentamethylene sulphide. The thiophenes were most resistant to oxidation, ring scission in this case requiring a large excess of active oxygen. Benedict[11] reports desulphurizing hydrocarbons in the vapor phase by the use of oxygen (air) and ammonia over a catalyst of activated carbon. Temperatures higher than 120°C. are necessary. An oxidation promoter such as pyridine or hydroquinone may be added to the hydrocarbon oil treated, according to Chebotar.[12] As little as 0.05 to 0.3 per cent is sufficient, and the distillate is then treated with air in the presence of an oil-soluble manganese, copper, cobalt or nickel soap.[13]

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[7] W. M. Cross, U. S. P. 1,969,502, Aug. 7, 1934, to Gasoline Products Co.; *Chem. Abs.*, 1934, **28**, 6294; *J. Inst. Pet. Tech.*, 1934, **20**, 577A.

[8] B. L. Rose, U. S. P. 2,028,922, Jan. 28, 1936, to Standard Oil Co. of Ohio; *J. Inst. Pet. Tech.*, 1936, **22**, 165A; *Chem. Abs.*, 1936, **30**, 1994.

[8a] U. B. Bray and L. B. Beckwith, U. S. P. 2,029,290, Feb. 4, 1936, to Union Oil Co. of Calif.; *J. Inst. Pet. Tech.*, 1936, **22**, 165A; *Chem. Abs.*, 1936, **30**, 1994.

[9] E. G. Ragatz, U. S. P. 2,029,504, Feb. 4, 1936, to Union Oil Co. of Calif.; *J. Inst. Pet. Tech.*, 1936, **22**, 165A; *Chem. Abs.*, 1936, **30**, 1994. For a discussion of the properties of asphalts, see Chapter 51.

[10] E. G. M. R. Légé, U. S. P. 2,038,369, April 21, 1936; *J. Inst. Pet. Tech.*, 1936, **22**, 267A, *Chem. Abs.*, 1936, **30**, 4000; British P. 432,368, 1935; *Chem. Abs.*, 1936, **30**, 279; *Brit. Chem. Abs.* **B**, 1935, 892.

[10a] J. Herzenberg, *Proc. World Pet. Congr.*, 1933, **2**, 30; *J. Inst. Pet. Tech.*, 1934, **20**, 98A; *Chem. Abs.*, 1934, **28**, 3566; *Brit. Chem. Abs.* **B**, 1934, 1044.

[11] W. L. Benedict, U. S. P. 1,971,172, Aug. 21, 1934, to Universal Oil Products Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 538A; *Chem. Abs.*, 1934, **28**, 6295.

Morrell and Egloff[14] suggest that sulphur dioxide and oxygen be mixed and used in the treatment of cracked distillates. These investigators treated a cracked California distillate with 4 pounds of sulphur dioxide per barrel, a slight excess of oxygen over that required to oxidize the sulphur dioxide, and about 2 pounds of steam per barrel. Temperatures of 120 to 315°C. are recommended in this treatment, and the vapors are contacted with solid catalysts such as clay, or with a finely divided metallic salt (e.g., zinc sulphate) on a support of fuller's earth. Under such conditions, the distillate showed a reduction in sulphur content of from 0.25 per cent to 0.1 per cent. These investigators have also suggested using oxygen and phosphoric acid in the presence of a non-metallic contact agent such as fuller's earth for removing sulphur.[15]

Harris[16] reports removing the haze-forming constituents of lubricating oils by an oxidation process. The oils are treated with air at 150 to 260°C. for a time sufficient to oxidize about 5 per cent of the oil. The product of this treatment is then dewaxed in the usual manner.[17]

Oxygen is used in some refining processes to revivify the refining agent. Peterkin[18] suggests, for instance, that if cupric chloride, lead sulphide or mercuric chloride is used as the refining agent, the catalyst can be revivified by treatment with air. Peck and Kleiber[19] have proposed a refining method involving two cracking zones. In the first of these, an oil stream is conducted through a pipe which is externally heated to a temperature of approximately 455°C. At this temperature, the oil is maintained under superatmospheric pressure, and no substantial decomposition of the hydrocarbons occurs. In the second zone, preheated oxygen or air is introduced into the heated oil. Partial combustion ensues, which rapidly raises the temperature of the material to 500-600°C. Thus, a Mid-Continent gas oil was heated to approximately 455°C., when about 3 per cent cracking to gasoline took place. At this point, air preheated to 455°C. was introduced into the oil in the ratio of approximately 15 cubic feet of air per gallon of oil. The partial combustion of the oil raised the temperature to about 540°C. A 30 per cent conversion to gasoline of good antiknock rating was reported. It is said that this method of cracking reduced the loss to gases and tar by about 50 per cent.

Kirsanov and Suslina[20] have studied the effect of ozone on gasolines from Chusov crudes. They report that by ozonization a practically sulphur-free gasoline can be obtained. The best results were procured when the ozonized product was distilled over lime in the presence of steam. The ozonization was conducted at −20°C., at which temperature the sulphur compounds are said to be converted into sulphuric acid, acidic non-volatile products, and neutral non-volatile compounds. The investigators report that ozonization tends simultaneously to lower the iodine number, however, and increase the paraffin and aromatic content at the expense of the naphthenes. From the desulphurization curves obtained, it appeared that the gasoline contained three general types of sulphur compounds reacting with the ozone at different rates. They believed that the sulphur compounds were largely derivatives of naphthenes and aromatics. It was suggested that an approximate picture of the number and type of substances contained in the mixture could be deduced from the desulphurization curves obtained in this ozonization. Morrell and Egloff[21] report a desulphurization process employing ozone. They suggest that the hydrocarbon vapors to be treated be passed over a bed of finely divided contact material such as sand, clay, fuller's earth or inert silicates together with a small amount of ozone (ten cubic feet of ozonized air per barrel of condensed hydrocarbon). At the same time, an alkaline solution (e.g., sodium plumbite, zincate or aluminate) runs countercurrently to the gases.

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[12] L. P. Chebotar, U. S. P. 2,036,396, April 7, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 3626; *J. Inst. Pet. Tech.*, 1936, **22**, 266A.

[13] The sulphur content of hydrocarbon gases used in bright-annealing furnaces can be removed by oxidation. (See, for example, A. G. Lobley, (British P. 429,402, 1935, to Birmingham Electric Furnaces Ltd.; *Brit. Chem. Abs.* **B**, 1935, 955; *Chem. Abs.*, 1935, **29**, 7267.) In this case the gases are mixed with sufficient air to burn the sulphur to sulphur dioxide and hydrogen sulphide, the gases are cooled, and the sulphur dioxide and hydrogen sulphide permitted to react to precipitate sulphur. The partly purified gases are then passed over an absorbent (calcium oxide or sodium carbonate) to remove the excess of sulphur dioxide.

[14] J. C. Morrell and G. Egloff, U. S. P. 1,979,565, Nov. 6, 1934, to Universal Oil Products Co.; *Chem. Abs.*, 1935, **29**, 334; *J. Inst. Pet. Tech.*, 1935, **21**, 65A. See also U. S. P. 1,947,868, Feb. 20, 1934; *Brit. Chem. Abs.* **B**, 1935, 10; *Chem. Abs.*, 1934, **28**, 2888.

[15] J. C. Morrell and G. Egloff, U. S. P. 1,946,095, Feb. 6, 1934, to Universal Oil Products Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 332A; *Chem. Abs.*, 1934, **28**, 2516.

[16] J. M. Harris, U. S. P. 2,025,387, Dec. 24, 1935, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1936, 822; *Chem. Abs.*, 1936, **30**, 1554; *J. Inst. Pet. Tech.*, 1936, **22**, 104A.

[17] See Chapter 1 for a discussion of dewaxing methods.

[18] A. G. Peterkin, Canadian P. 344,365, 1934, to Atlantic Refining Co.; *Chem. Abs.*, 1935, **29**, 2344.

[19] E. B. Peck and C. E. Kleiber, U. S. P. 1,981,826, Nov. 20, 1934; *Chem. Abs.*, 1935, **29**, 590; *J. Inst. Pet. Tech.*, 1935, **21**, 64A.

[20] A. V. Kirsanov and V. N. Suslina, *J. Applied Chem.* (*U.S.S.R.*), 1935, **8**, 277; *Brit. Chem. Abs.* **B**, 1935, 709; *J. Inst. Pet. Tech.*, 1936, **22**, 100A; *Chem. Abs.*, 1936, **30**, 3977.

Darrah[22] has made the suggestion that hydrocarbon oils be treated with oxygen in a type of electrolytic cell wherein the electric current supplies both the oxygen, and by the resistance to its flow, the heat needed in the transformation. The oil (kerosene or fuel oil) is suspended in an electrolyte, such as a soap solution and passed through a restricted opening. An electric current of relatively high density is passed through the solution at this point, strongly heating the liquid and at the same time releasing oxygen for the formation of oxidation products.

OXIDIZED MOTOR FUELS

Ellis[23] has found that gas oil, cracked and subsequently oxidized, may be made to yield a gasoline of high antiknock value. In this process, the oil is first cracked (at about 400°C.) under 250 to 350 pounds per square inch pressure and transferred to a "soaking tank" maintained at a similar temperature. The hot, cracked vapors from this tank are passed to an oxidizing chamber, where oxygen is admitted at a number of points but in quantities sufficiently small so as to prevent the formation of an explosive mixture (sufficient only to oxidize 5 to 10 per cent of the hydrocarbon vapors). The reaction may be carried out in part, he finds, by admitting a small part of the oxygen to the "soaking tank." This is not as satisfactory as oxidation in the separate reactor, however, since the temperature and other conditions in this part of the apparatus are determined as best for cracking reactions rather than oxidation. The oxidation reactor is best maintained at a temperature of 120° to 240°C. From the oxidized products, a gasoline fraction is obtained. This distillate may include higher ends than are ordinarily permissible, due to the high antiknock rating resulting from the partial oxidation. Cracked gasoline consists essentially of a complex mixture of paraffinic, olefinic, aromatic and naphthenic compounds. Of these, olefins tend to carbon deposition upon combustion, and aromatics effect a suppression of the knocking tendencies of the fuel. Ellis[23a] proposes to oxidize olefinic and dehydrogenate naphthenic compounds in a single operation by treating distillation vapors from cracked gas oil with air. During the period of contact of the hydrocarbon vapors and air, the temperature of the reactants is held at 205-215°C. and the pressure at 3-4 atmospheres. Thus a fuel containing a large proportion of aromatics and a small percentage of olefins is said to be secured.

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[21] J. C. Morrell and G. Egloff, U. S. P. 1,957 794, May 8, 1934, to Universal Oil Products Co.; *J. Inst. Pet. Tech.*, 1934, **20**, 459A; *Chem. Abs.*, 1934, **28**, 4218.

[22] W. A. Darrah, U. S. P. 2,045,343, June 23, 1936; *Chem. Abs.*, 1936, **30**, 5511.

[23] Carleton Ellis, U. S. P. 1,976,696, Oct. 9, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1934, **28**, 7483, *Brit. Chem. Abs.* **B**, 1935, 838.

[23a] Carleton Ellis, U. S. P. 2,077,994, April 20, 1937, to Ellis-Foster Co.; *Chem. Abs.*, 1937, **31**, 4104.

Burk and Hughes[24] have suggested that the antiknock value of fuel may be increased by treating a straight-run gasoline at 450 to 700°C. in the presence of ½ to 5 volumes of air per volume of gasoline vapor, for 0.075 to 1 second under 100 pounds per square inch pressure. If the conditions are held close to 500°C. with a contact time of 0.7 seconds and an air-to-fuel ratio of approximately 1:1 used, the conversion is said to take place without substantial change of the boiling point characteristics.

It has been found that a naphtha of unsatisfactory knock rating can be blended with a cracking-coil tar and treated with oxygen to produce a satisfactory motor fuel. Burk[25] reports that the hydrocarbon tar, too heavy for use as a motor fuel, will react with oxygen and the lighter hydrocarbon material if the two hydrocarbon mixtures are preheated to 370° to 600°C. and then subjected to the action of a controlled amount of oxygen. The reaction is carried out under 10 to 150 pounds per square inch pressure. An analogous process has been suggested by this investigator for producing motor fuel from gas oils. The hydrocarbon is heated to a cracking temperature while under pressure in a pipe or coil. The pressure is then released, and the hydrocarbon is atomized in the presence of air while at a temperature of 600°C. The contact with air lasts from 1.5 to 25 seconds, and a pressure of 10 pounds per square inch is maintained in this reactor to effect the conversion into motor fuel. It is also possible to lower the boiling point of hydrocarbon materials by an oxidation process. Thus Ellis[26] has described a process of preparing an oxidized kerosene or gasoline from a heavier fuel. The raw material (e.g., kerosene) is passed through a cracking tube heated to 540° to 590°C. and thence to a trap, wherein the very heavy products are removed. The vapors and fixed gases then pass into a mixing chamber, where they are mixed with air. The mixture of oil vapors and air is then passed over a catalyst of pumice fragments impregnated with vanadium oxide. This catalyzer is contained in a U-tube of sheet steel, immersed in a bath of molten lead. The temperature of the lead bath is held at 425° to 430°C. The resulting vapors are passed first through a water scrubber, then an oil scrubber, and finally over silica gel. The oxidized material so obtained is blended with pressure-still or natural gasoline, or a blend of the three is prepared for use as an antiknock motor fuel.

A process suggested by Chappell[27] also combines the lowering of boiling point with increase of antiknock value. The oil is heated to a cracking temperature (425° to 700°C.), under pressure (up to 1000 pounds per square inch), and passed into a reaction chamber. Unvaporized oil is withdrawn from this chamber, and oxygen-containing gas (air), preheated to the temperature of the oil, is admitted. The amount of oxygen admitted is so regulated as to reduce the hydrogen content of the oil vapor to approximately 14.3 per cent. The reaction products are fractionated and a motor-fuel fraction obtained which is reported to have a high antiknock value. The unvaporized oil and the higher oxidized fractions are blended to produce a heavy fuel oil.

The oxygen required for the partially oxidized motor fuels may, it is reported, be supplied by substances other than air. Thus, a mixture of heavy crude oil, 2 per cent of chromic acid mixture, and half of 1 per cent of a catalyst such as manganese dioxide or barium peroxide, may be agitated together and allowed to stand. After 24 hours, the upper, clear solution is decanted from the precipitate and used as a substitute for gasoline.[28]

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[24] R. E. Burk and E. C. Hughes, U. S. P. 1,997,480, April 9, 1935, to Standard Oil Co. of Ohio; *Brit. Chem. Abs.* **B**, 1936, 358; *Chem. Abs.*, 1935, **29**, 3821; *J. Inst. Pet. Tech.*, 1935, **21**, 220A.

[25] R. E. Burk, U. S. P. 1,963,647, June 19, 1934, to Standard Oil Co. of Ohio; *Chem. Abs.*, 1934, **28**, 5222; *J. Inst. Pet. Tech.*, 1934, **20**, 501A

[26] Carleton Ellis, U. S. P. 1,973,475, Sept. 11, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1934, **28**, 6997; *Brit. Chem. Abs.* **B**, 1935, 713.

[27] M. L. Chappell, U. S. P. 2,002,729, May 28, 1935; *Brit. Chem. Abs.* **B**, 1936, 486; *Chem. Abs.*, 1935, **29**, 4932.

James and Zeisenheim[29] studied the properties of some oxidized fuels (kerosene and gasoline) of this type and report that, although the gross thermal value of the oxidized material is about one-eighth less than that of the hydrocarbon from which it derived, other factors may offset this. They believe, however, that greater energy is available in an internal combustion engine powered by these fuels. This paradoxical result was due, they suggest, to the fuel molecules being weakened to oxidation attack (in the internal combustion engine) because of their oxidized character. This is considered to result in a better "clean up" and more propulsive effort during combustion.

Oxidation of still vapors from a cracked oil results in the formation, in addition to partially oxidized gasoline, of acids and aldehydes which may impart an objectionable odor to the fuel. Removal of these constituents may be brought about by hydrogenation, polymerization, or by the addition of phenols to form synthetic resins.[29a] In one procedure, kerosene was allowed to drip into a cracking furnace at 1200-1300°F. The cracked vapors issuing from the furnace were partially condensed to separate the heavier portions. Uncondensed vapors and air were then admixed and led into a reaction chamber containing a promoter of iron coated with vanadium oxide. Oxidation was effected at 800-1000°F., and the liquid products collected by condensation. The latter consisted of two layers, the upper containing oxidized gasoline, the lower an aqueous solution of acids and aldehydes. Phenol was then incorporated in the aqueous layer together with a condensation catalyst to furnish a synthetic resin.

PRODUCING FUEL GAS FROM HYDROCARBON OILS

Some years ago[30] (1913) it was proposed that a fuel vapor for use in an internal combustion engine might be prepared by forcing a jet of a hydrocarbon oil such as kerosene through a flame. The finely divided fuel is simultaneously raised to a high cracking temperature and partially oxidized, and these resultant vapors collected. It is said that the vapors so produced are well suited to rapid or instantaneous combustion, and do not deposit carbon in the engine consuming them. The apparatus is so designed that the flame is unable to strike back along the fuel vapors by reason of metal screens which rapidly lower the temperature of the vapors below the ignition point. The apparatus is maintained at less than atmospheric pressure by the intake manifold vacuum of the associated engine. At intermediate points between the cracking and oxidizing flame and the internal combustion engine, but beyond the point where the flame is effectively extinguished, heated air is introduced. The fuel vapor so produced is relatively persistent, being composed largely of permanent gases, and though it cannot be stored or piped long distances, it is sufficiently stable that it may be piped, for instance, across a yard or across a street. In contrast, however, Perry[31] reports that a commercially distributable gas may be produced by an oxidation-cracking process. This process uses refinery gases as raw material, however, conducting gases and oxygen in separate streams to a reaction zone. The oxygen is introduced into the center of the stream of hydrocarbon gas in such a manner that it is completely surrounded by the oil gases. Partial combustion ensues, the intense heat of the oxidation serving to crack the remainder of the hydrocarbon. The combustion takes place in an enclosed chamber, and the resulting products are said to form a gas mixture having specific density and calorific power closely approximating those of carbureted water-gas.

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[28] Kanejiro Ueda and Aoi G. K., Japanese P. 100,757, 1933; *Chem. Abs.*, 1934, **28**, 3575.

[29] J. H. James and F. C. Zeisenheim, *Chem. and Met. Eng.*, 1923, **28**, 543, *Chem. Abs.*, 1923, 17, 2041; *J.S.C.I.*, 1923, **42**, 391A.

[29a] Carleton Ellis, U. S. P. 2,079,607, May 11, 1937, to Ellis Foster Co.

[30] A. T. Porter and H. E. Rider, U. S. P. 1,064,086, June 10, 1913, to Oil Utilities Company; *J.S.C.I.*, 1913, **32**, *743*. See also British P. 10,047, 1913; *Chem. Abs.*, 1914, **8**, 3501. An analogous process for making an internal combustion engine fuel from even heavier hydrocarbons was suggested by E. B. Benham (U. S. P. 1,000,768, Aug. 15, 1911, to Hydrocarbon Converter Co.; *Chem. Abs.*, 1911, **5**, *3727*) who proposes a system of heated contact zones. The hydrocarbon oil (a crude from which the lighter fractions have previously been removed) is injected with a stream of air into a reaction chamber made of clay or siliceous material. The fuel droplets impinge on a refractory surface at a temperature of 600° to 800°C., the partial combustion of the hydrocarbon aiding in maintaining this temperature. The cracked vapors are then led through a further high temperature zone that the cracked molecules may become stabilized. In this apparatus, too, the vacuum created by the internal combustion engine aids the circulation of the vapors. In starting the apparatus, and as an aid in maintaining the high temperatures required, the hot exhaust gases of the internal combustion engine are circulated about the cracking apparatus. The engine is started on gasoline originally.

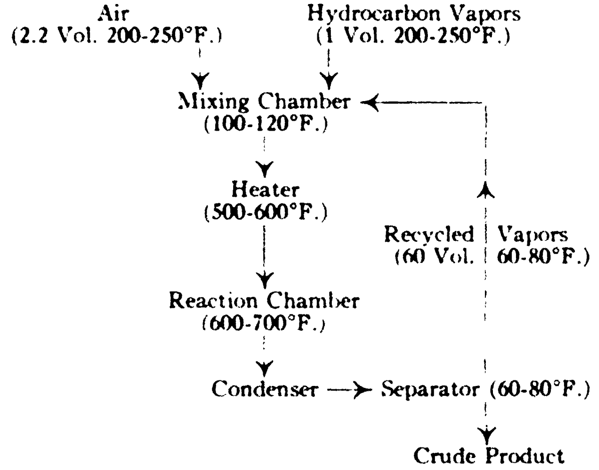

FIG. 250A. Flow Diagram for Controlled Oxidation of Gaseous Hydrocarbons to Alcohols and Other Oxygenated Products. (C. L. Thompson, T. S. Bacon and J. E. Bludworth)

If a hydrocarbon oil is burned with a limited supply of oxygen and under proper conditions, a mixture of carbon monoxide and hydrogen is obtained, it is reported. The temperature of this reaction, of course highly exothermic in nature, can be controlled, however, by the addition of a regulated supply of steam to the entering gases, along with a further quantity of oil. The reaction ensuing between the oil and water vapors at the high temperature produces further carbon monoxide and hydrogen by an endothermic reaction. The resultant mixture is, finally, practically pure carbon monoxide and hydrogen. This product may be enriched by the addition of hydrocarbon illuminants if it is desired as a general fuel gas.[32] Maier[33] points out that such mixtures of hydrogen and carbon monoxide can be made also by non-inflammatory reaction if a catalyst is employed and high gas velocities maintained. He suggests, for example, that a properly proportioned hydrocarbon-oxygen mixture be passed over a catalyst of nickel on aluminum oxide maintained at a sufficiently high temperature to initiate the reaction. The gases pass

[31] J. A. Perry, U. S. P. 1,971,728, Aug. 28, 1934, to United Gas Improvement Co.; *Chem. Abs.*, 1934, **28**, 6553; *Brit. Chem. Abs.*, **B**, 1935, 757.

[32] British P. 416,957, 1934, to Carburetted Gas, Inc.; *Brit. Chem. Abs.* **B**, 1934, 1047; *J. Inst. Pet. Tech.*, 1934, **20**, 617A; *Chem. Abs.*, 1935, **29**, 1613.

[33] C. G. Maier, U. S. P. 2,039,603, May 5, 1936, to Mountain Copper Co., Ltd.; *Chem. Abs.*, 1936, **30**, 4278.

over the catalyst at a velocity sufficient to prevent flame. This velocity falls gradually, although it is always great enough to prevent inflammation. The product gases are reported to be substantially free of carbon dioxide, water vapor and unreacted hydrocarbon. This investigator[34] suggests that an apparatus for the oxidation be arranged in such a manner that a high velocity stream of preheated air picks up a side stream of hydrocarbon gas, and the mixture passes into a catalyst chamber. This chamber contains a porous catalytic mass, and is parabolic in shape, allowing the gases to expand as they pass through. The stream of gas on entering the catalyst is deflected by a crucible-shaped, non-porous baffle. Ray[35] has suggested a catalytic method for removing unreacted oxygen from large volumes of gas, wherein the oxygen constitutes less than 4 per cent of the composition. The gas mixture is brought in contact with a highly reactive mass of carbon kept at a temperature of approximately 600°C. for a short, regulated time. The time of contact is controlled to allow the reaction of the oxygen with the carbon to form only carbon monoxide. Walker,[36] on the other hand, proposes a method for accomplishing removal of small percentages of oxygen from large volumes of gas which involves the addition of further oxygen as the first step. The amount of oxygen to be added is determined by the amount already present; the total amount is fixed by the reaction conditions to be maintained. The total amount is to be such that when passed over a catalyst (platinum, manganese dioxide or cupric oxide) at a high temperature, reaction shall ensue, consuming all the oxygen present and liberating sufficient heat of combustion to maintain the catalyst at the desired temperature.

PRODUCTION OF ALCOHOLS AND ACIDS

The production of hydrogen and carbon monoxide by oxidation of hydrocarbon oils and gases is of growing importance in the production of methyl alcohol, produced synthetically by the condensation of these two gases. This type of synthesis will be discussed under the reactions of carbon monoxide and is beyond the scope of the present chapter.[36a] The reaction of oxygen with the lighter hydrocarbons of refinery gases has been found to produce considerable quantities of methanol, accompanied, however, by other and more completely oxidized products. It has been proposed that a mixture be prepared consisting of 0.5 to 3 per cent oxygen (by the addition of the corresponding volume of air), 10 to 40 per cent refinery gases, and sufficient exhaust gases from the process to make up 100 per cent. This mixture is heated to about 370°C. under 250 pounds per square inch pressure. These conditions are maintained for a sufficient period of time to permit complete combination of the oxygen, and the resulting vapors are then cooled. The uncondensed portions are recirculated in the process chambers.[37] Cristescu[38] reported a method whereby methane and carbon monoxide or dioxide might be reacted to produce alcohols. The mixed gases are passed through boiling water containing a catalyst, such as wood charcoal and a metal oxide (e.g., cupric oxide, lead dioxide or zinc oxide). The resulting gases are then passed through a reaction chamber containing a further catalyst of wood charcoal washed with sodium hydroxide.

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[34] C. G. Maier, U. S. P. 2,022,778, Dec. 3, 1935, to T. B. Swift; *Brit. Chem. Abs.* **B**, 1936, 969; *Chem. Abs.*, 1936, **30**, 825.

[35] A. B. Ray, U. S. P. 2,019,632, Nov. 5, 1935, to Carbide and Carbon Chemicals Co.; *Chem. Abs.*, 1936, **30**, 584.

[36] J. C. Walker, U. S. P. 1,960,212, May 22, 1934, to Empire Oil and Refining Co.; *Brit. Chem. Abs.* **B**, 1935, 373; *Chem. Abs.*, 1934, **28**, 4573.

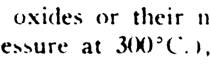
[36a] See Chapter 52.

[37] C. L. Thompson, T. S. Bacon and J. E. Bludworth, U. S. P. 2,004,714, to Hanlon-Buchanan Inc.; *Chem. Abs.*, 1935, **29**, 5123, *Brit. Chem. Abs.* **B**, 1936, 632

[38] J. Cristescu, French P. 770,223, 1934; *Chem. Abs.*, 1935, **29**, 474, also British P. 427,221, 1934; *Brit. Chem. Abs.* **B**, 1935, 618; *Chem. Abs.*, 1935, **29**, 6245.

On the other hand, Penniman[39] has reported making higher alcohols, aldehydes, ketones and other similar oxidized products by a direct oxidation of residual oils from cracking stills. In this process a stream of the hydrocarbon is preheated to 150°-370°C. and passed into a converting vessel under pressure substantially greater than atmospheric. Air is admitted to this chamber, and the partial combustion maintains a temperature here of approximately 400°C. The resultant vapors are removed and the less volatile constituents returned to the reaction zone. Preheating of these liquids is unnecessary. The vapors are fractionated to recover motor fuels and the mixed oxidized compounds, largely alcohols, ketones and aldehydes of higher molecular weight.

Carpenter[40] reports a further carbon monoxide reaction of the lower alcohols, such as methanol, by which the next higher aliphatic acid is produced. Methanol and carbon monoxide are reacted in the presence of a catalyst such as chromic or tungstic acid, under 700 atmospheres pressure and at a temperature of 300°C. The carbonyl group adds to the molecule, producing acetic acid. Woodhouse[41] reports an analogous reaction, involving the treatment of methyl alcohol and carbon monoxide in the presence of silicon, magnesium, aluminum, titanium, zirconium or tungsten oxides or their mixtures. Similar conditions are used (i.e., 700 atmospheres pressure at 300°C.), but under the influence of these catalysts, other compounds such as methyl formate and methyl acetate are formed, as well as acetic acid. The process has been investigated by a number of workers and various catalysts proposed. Some recommend the addition of a diluent such as nitrogen or water vapor to the reactive vapors. Inorganic polybasic acids (e.g., phosphoric and arsenic acids) have been suggested as catalysts[42] as well as a complex silica-phosphate $[SiO(PO_3)_2]$ which can be revived by the action of phosphoric acid.[42a] Woodhouse[43] reports that halogens, hydrohalides, alkyl halides and nitrogen oxides serve as accelerators in such reactions as that producing acetic acid from methyl alcohol and carbon monoxide and in a number of other reactions involving carbon monoxide.

A different type of reaction producing acids from alcohols has been proposed by Hale.[44] This reaction involves dehydrogenation of the alcohol with the intermediate formation of the corresponding aldehyde, and the subsequent addition of a molecule of water to form a dihydroxy compound. In the presence of a basic salt of an amphoteric salt-forming metal and an organic acid (i.e., such a salt as hydroxy manganese acetate,  $HOMnO\underset{\underset{O}{\|}}{C}\text{-}CH_3$) the dihydroxy compound reacts to form the diacetate and water. The series of reactions, then, is as follows:

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[39] W. B. D. Penniman, U. S. P. 2,044,014, June 16, 1936; *Chem. Abs.*, 1936, **30**, 5403; *J. Inst. Pet. Tech.*, 1936, **22**, 411A

[40] G. B. Carpenter, U. S. P. 2,021,127, Nov. 19, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 490. See also British P. 428,450, 1935, to H. A. Patterson; *Brit. Chem. Abs.* **B**, 1935, 665; *Chem. Abs.*, 1935, **29**, 6906.

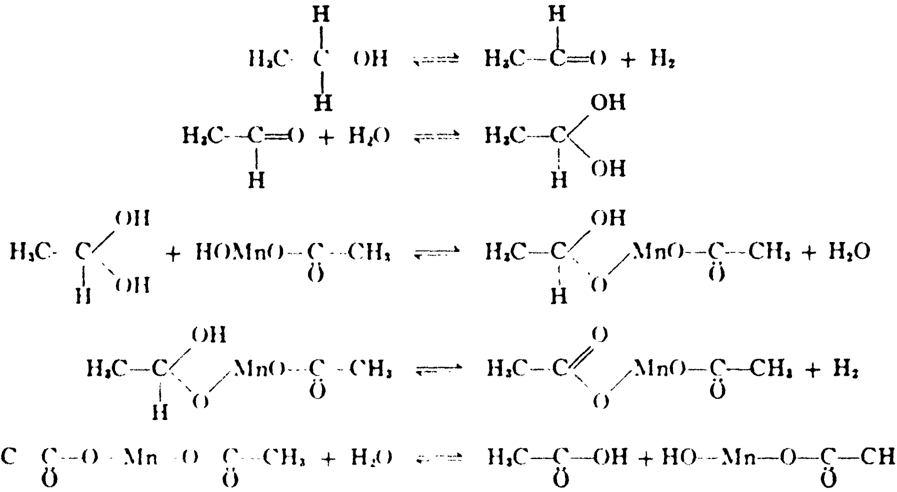
[41] J. C. Woodhouse, U. S. P. 2,019,754, Nov. 5, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 490.

[42] G. B. Carpenter, U. S. P. 1,979,449 and U. S. P. 1,979,450, Nov. 6, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 939; *Chem. Abs.*, 1935, **29**, 179. See also D. V. N. Hardy, *J. C. S.*, **1934**, 1335; *J. Inst. Pet. Tech.*, 1934, **20**, 564A; *Chem. Abs.*, 1935, **29**, 116.

[42a] R. L. Brown, U. S. P. 1,967,189, July 17, 1934, to Atmospheric Nitrogen Corp.; *Brit. Chem. Abs.* **B**, 1935, 442; *Chem. Abs.*, 1934, **28**, 5833.

[43] J. C. Woodhouse, U. S. P. 2,003,477, June 4, 1935, to E. I. du Pont de Nemours & Co., *Chem. Abs.*, 1935, **29**, 4854.

[44] W. J. Hale, U. S. P. 2,027,378, Jan. 14, 1936; *Chem. Abs.*, 1936, **30**, 1384.



In summation of the five sets of equilibria, one molecule of alcohol plus two molecules of water yield one molecule of acid, one molecule of water and two molecules of hydrogen. Theoretical 100 per cent efficiency would reduce this to an interaction of one molecule of water and one molecule of alcohol to yield one molecule of acid and two of hydrogen, the water serving as the oxidizing agent.

The catalyst employed must be a salt of a metal capable of forming amphoteric hydroxides, reacting with organic acids to yield basic salts which resist complete hydrolysis under the action of water at a temperature of 350°C. At the same time, a dehydrogenating catalyst must be present, and the presence of free hydrogen must not reduce the amphoteric metal oxide to the free metal. These conditions so limit the choice of metals, Hale states, that only beryllium, copper, magnesium, zinc, aluminum, zirconium, the cerium metals, chromium, manganese, iron and cobalt compounds reacted satisfactorily. Of these, the basic salts of iron, cobalt, copper and zinc were limited to relatively low temperature conditions, owing to the high hydrogen concentrations obtained. The dehydrogenating catalyst to be incorporated in the catalyst mass may consist of metallic copper, silver, zinc, palladium, or other platinum metals.

The concentration of hydrogen resulting from the reaction should be removed, Hale finds, in order to prevent its tendency to reverse the equilibrium. This may be accomplished, he suggests, by the use of a membrane selectively porous to hydrogen, such as a thimble of sillimanite. The temperature conditions maintained may lie between 150° and 350°C., but optimum results were obtained at 260° to 280°C. The primary reaction of dehydrogenation is endothermic, however, and the fore part of the reaction tube may advantageously be maintained at a somewhat higher temperature than the after section. Thus, using 46 grams (one mole) of ethanol, and 2 moles of water over a catalyst composed of copper, manganous and aluminum salts and copper metal at an entering temperature of 300°C. and an efflux temperature of 260° to 280°C., the following results were obtained:

Product	Grams
Acetic Acid (52.6% concentration)	30
Acetaldehyde	21.5
Ethyl Acetate	0.3
Hydrogen	3.0
Water	27.0

By recycling the acetaldehyde fraction, the concentration of acetic acid was raised to 75 per cent.

This process is said to be advantageous in that it yields a product containing concentrated acid, and, during the oxidation, no explosive mixture is formed. It may be applied equally to ethylene, or higher homologs, or higher alcohols such as butanol.

A cyclic method of producing the corresponding acid from one of the lower alcohols suggested by Hale and Haldeman[45] produces the aldehyde as an intermediate step. In this process, the alcohol (e.g., ethanol) is passed over a dehydrogenating catalyst to form the corresponding aldehyde and free hydrogen.

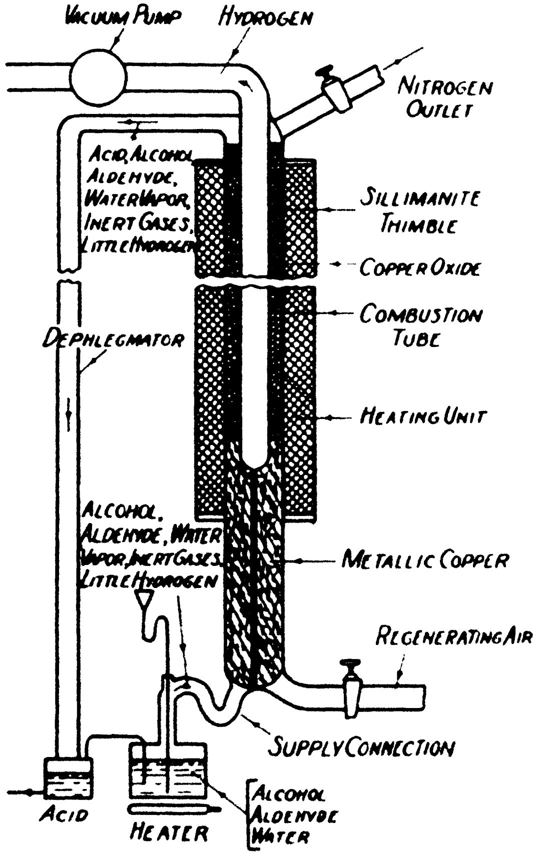


FIG. 251. Sketch of Apparatus for Oxidation of Alcohols to Aliphatic Acids. (W. J. Hale and W. S. Haldeman)

The reaction mixture is then passed over a surface made of a material such as sillimanite which is permeable to hydrogen, and part of the hydrogen is separated in this way. The mixed aldehyde-containing vapors then contact a readily reducible oxide, such as cupric oxide, at a temperature between 150° and 350°C., and are oxidized to the corresponding acid and water. The acid is separated from the mixed products, the remaining vapors mixed with further alcohol, and the mixture recycled through the system (See Fig. 251).

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[45] W. J. Hale and W. S. Haldeman, U. S. P. 1,951,280, March 13, 1934; *Chem. Abs.*, 1934, **28**, 3416; *Brit. Chem. Abs.* **B**, 1935, 138.

It is frequently found that the recovery of petroleum oxidation intermediates in fair degree of purity is difficult, and this property can be used to advantage in the production of alcohol denaturants. James[46] suggests that a liquid hydrocarbon be vaporized, mixed with air and passed through a contact zone at a temperature of 180° to 500°C. The contact catalysts employed are oxides of metals having variable valency, such as the blue oxides of molybdenum. The vaporous products are condensed, yielding a complex liquid mixture of partial oxidation products ranging from alcohols through aldehydes to aldo-fatty acids. The percentage of the various chemical substances composing the final mixture may be varied by control of such conditions as the reaction temperature, time of contact, and whether or not steam or other diluent is added to the gases before reaction. James reports that alcohols, aldo-alcohols, aldehydes, ketones, aldo-acids, aldo-hydroxy acids, keto-acids, hydroxyketo-acids, and mixed esters of these compounds, both normal esters and lactonic-type esters, are present in the condensed product. In addition there are present ethers, both of the normal type and of the inner or "bridge" type. Some unchanged hydrocarbons pass through, as well as fractions consisting largely of highly unsaturated compounds possessed of persistent and penetrating odors. This complex mixture is neutralized by the addition of either caustic alkali or a lime slurry, and the neutral product remaining extracted with alcohol. The alcohol is said to selectively dissolve out the more highly oxidized constituents of the mixture, and by regulating the amount of water incorporated with the alcohol, effective separation of two liquid layers is secured. A distillation step separates a portion of the oxidized mixture having a distillation curve close to that of alcohol, resulting in a denaturant which, it is said, cannot be removed from the alcohol by chemical or physical means short of the destruction of the alcohol.

That effective denaturants difficult to separate from the denatured substance can be produced from partially oxidized hydrocarbons indicates the complexity of the problem facing the investigator who seeks to derive pure compounds by this partial oxidation. Primarily, the problem is naturally somewhat simplified by so choosing conditions of reaction as to minimize the formation of these complex mixtures rather than to favor them. Numerous methods of separation have been suggested, however, such as the solvent extraction suggested by James.[47] He reports that the more highly oxidized products can be separated from the less oxygenated substances (in the range of alcohols to organic acids) by an extraction with liquid sulphur dioxide. Thus the partial oxidation products of a hydrocarbon fraction such as gasoline may be condensed and the cooled liquid treated with liquid sulphur dioxide. The fractional extraction is controlled by the temperature (always below the boiling point of the sulphur dioxide extraction agent) at which the process is carried out.

SOLVENTS, DRYING OILS AND VARNISHES

The partial oxidation products of light hydrocarbon distillates have been suggested as solvents for various uses, but James[48] finds that these frequently have powerful, and usually objectionable, odors due in large part to various aldehydic compounds. He reports that this odor can be largely eliminated by a treatment with alcohol and calcium chloride. The addition of these materials in anhydrous form brings about a condensation of the odoriferous aldehydes to less pungent acetals. These, in turn, can be extracted with 70 per cent ethyl alcohol which acts as a selective solvent for the more highly oxidized components of such a complex mixture to leave a solvent which is said to be almost odorless.

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[46] J. H. James, U. S. P. 2,009,661, July 30, 1935, to Clarence P. Byrnes; *Chem. Abs.*, 1935, **29**, 6358. See also W. P. Bitler, U. S. P. 1,948,161, Feb. 20, 1934, to C. P. Byrnes; *Brit. Chem. Abs.* **B**, 1934, 1094; *Chem. Abs.*, 1934, **28**, 2723..

[47] J. H. James, U. S. P. 1,970,535, Aug. 14, 1934, to C. P. Byrnes; *Chem. Abs.*, 1934, **28**, 6156; *Brit. Chem. Abs* **B**, 1935, 664.

[48] J. H. James, U. S. P. 1,907,822, May 9, 1933, to C. P. Byrnes; *Brit. Chem. Abs.* **B**, 1934, **86**; *Chem. Abs.*, 1933, **27**, 3761.

Instead of oxidizing the lower hydrocarbons to liquid compounds it has also been suggested that the higher hydrocarbons such as paraffin wax may be oxidized to produce esters suitable for use as plasticizing and softening agents for plastics containing cellulose derivatives and lacquers of this type. In this procedure paraffin wax is oxidized by nitric acid at 90°C., the concentration of nitric acid being maintained by adding gaseous nitric anhydrides. The oxidation product is esterified with butyl alcohol and the ester distilled off (at 170° to 230°C. under 1 or 2 mm. pressure). It is reported that if this ester is added to a solution of low-viscosity cellulose nitrate in a butyl acetate-butyl alcohol-toluene solvent, a lacquer yielding a durable film is formed.[49] Winning[50] suggests that a solvent be prepared by the partial oxidation of a "hydroformed solvent" (a product derived from the destructive hydrogenation of a petroleum fraction boiling in the gasoline range and up to 370°C.). Thus, a cracked hydrocarbon distillate boiling between 224° and 332°C. was obtained from a Mid-Continent crude. It was destructively hydrogenated at 510°C. under a pressure of 3000 pounds per square inch. A fraction of the product boiling below 200°C. was separated, and the remainder recycled. The material so obtained, was placed in a glass-lined bomb under 110 pounds pressure of air, and held at a temperature of 100°C. for 48 hours. The resulting oxidized product was reported to be an effective substitute for aromatic solvents such as benzene or toluene in preparing surface coatings.

That drying oils of various sorts could be made by partial oxidation of petroleum fractions has been known for some years. In 1867 DeGerbeth[51] reported making a drying oil suitable for paint and varnish making or oil-cloth production by oxidizing petroleum oils. In this process, 25 to 40 gallons of water were mixed with each ton of oil, and the whole blown with steam until reaching a temperature of 80° to 100°C. Oxidation was then brought about by the addition of hypohalites, perhalates or manganese dioxide. Agitation with steam and a drying agent was continued. Finally, the mixture was blown with air or ozonized air.

Woods[52] commented on the resemblance of the gums formed in cracked gasoline to linseed oil, and suggested that a drying oil could be made by oxidizing a vapor phase cracked Mid-Continent gas oil. A naphtha fraction boiling between 48° and 225°C. was oxidized for six hours at 100°C. under 100 pounds per square inch pressure of air. The sample was cooled, and distilled under vacuum to 6 per cent bottoms. The resemblance between the drying oil so prepared and commercial linseed oil was shown by the properties listed in Table 203.

TABLE 203. *Comparison of Natural and Synthetic Drying Oils.*

	Commercial Linseed Oil	Drying Oil from Cracked Gasoline
Gravity °A.P.I.	19.8	21.4
Iodine No.	186	180
Saponification No.	190	188

The two oils were compared as thinners in paints for use on both metal and wood surfaces. After 12 months exposure, the paint made with the oxidized cracked naphtha showed signs of cracking, however. The investigator believes that the proper treatment may be found which will produce a satisfactory oil, at considerable economic advantage.

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[49] British P. 395,340, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 483; *Brit. Chem. Abs.* **B**, 1933, 906. For further information regarding the oxidation of paraffin wax see Chapter 43.

[50] C. Winning, U. S. P. 2,068,834, Jan. 26, 1937; to Standard Oil Development Co.

[51] F. L. deGerbeth, British P. 3191, 1867

[52] G. M. Woods, *Petroleum Engineer*, 1936, **8**, No. 1, 106.

Pohl[53] described a process for producing driers for use in varnishes, lacquers and paints consisting essentially of heavy-metal water-insoluble soaps. These products are made by treating the mixed oxidation products of paraffin wax, or a similar wax, with cobalt acetate (at 100° to 140°C.) or with caustic soda solution. If the soda solution is used, the resultant soap is separated from unsaponifiable substances, and the organic radical precipitated by treatment (at an elevated temperature) with a metallic salt of an inorganic acid, such as manganous chloride, copper sulphate or aluminum sulphate. Fiore[54] reports producing a paint vehicle oil by oxidizing a mixture consisting of 80 per cent mineral oil and 20 per cent vegetable oil by passing ozone through the mixture (maintained at 100°C.) for 1 hour. The process is completed by adding a quantity of a 1:2 mixture of nitric acid and ethyl alcohol equal to about one-half the weight of the oil mixture. Instead of using an oxidized petroleum oil directly, Adal'yan[55] has found that the acid sludge produced in refining processes can be treated to procure a drying oil. The sludge is diluted with water and thoroughly agitated with air, the upper layer then being separated. It is agitated several times with water and neutralized with sodium hydroxide. The final product is reported to dry in 3 to 4 hours, forming a thin, elastic film.

It is reported that pentaerythritol esters of the acids obtained by oxidation of paraffin wax are useful in the preparation of varnishes. The esters are prepared by heating the oxidized paraffin acid (in the presence of catalysts) with pentaerythritol. Basic oxides or hydroxides, such as lead monoxide, calcium, or zinc oxide or sodium hydroxide, serve as catalysts. Inert diluents (e.g., nitrogen or carbon dioxide) may be present as well.[55a]

LUBRICATING OILS AND GREASES

King[56] has pointed out that an oil which has been oxidized may have greatly increased film strength. For instance, an oil capable of maintaining a film intact up to 160°C. in its ordinary state may, after oxidation, prove capable of maintaining lubrication up to 300°C. He offers the explanation that these oxidized oil molecules attach themselves to the lubricated metal surfaces by the oxidized, and hence activated, end. It has been shown that normal oil loses to some extent its "oiliness" (its ability to resist film-rupture) if run through clean glass or silica chips, since the polar substances which have the greatest power of gripping surfaces are left behind. Oil, so treated, regains its "oiliness," however, if left in contact with the air. On the other hand, in contact with nitrogen this recovery does not occur. It appears that the oxidized oil molecules have not only greater adhering strength, but their coherence is greater as well. Thus, the suggestion is made that on the first polar attachment to the lubricated metal a layer of coherent polar lubricant many molecules thick is built up. This condition would result in diminished rigidity, increased slip, and hence lower friction.

However, King reported that single-variety oils were able to show little improvement on oxidation. Blended oils (i.e., oils of different oxidation characteristics) increased in viscosity or maintained viscosity over long periods of oxidation, and their performance showed sustained improvement. The most satisfactory results were obtained with blends of easily oxidized varieties and those difficult to oxidize. Oxidation was then assumed to take place through the influence of the readily oxidized molecules.

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[53] F. Pohl, U. S. P. 1,900,734, March 7, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, **27**, 3094.

[54] G. Fiore, U. S. P. 2,020,936, Nov. 12, 1935; *Brit. Chem. Abs.* **B**, 1936, 801; *Chem. Abs.*, 1936, **30**, 632.

[55] L. K. Adal'yan, *Neft*, 1933, **4**, No. 10, 9; *Brit. Chem. Abs.* **B**, 1935, 1030; *Chem. Abs.*, 1935, **29**, 2711.

[55a] British P. 405,826, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 4922; *Brit. Chem. Abs.* **B**, 1934, 334.

[56] R. O. King, *J. Inst. Pet. Tech.*, 1934, **20**, 97; *Chem. Abs.*, 1934, **28**, 3572; *Brit. Chem. Abs.* **B**, 1934, 309.

It has been suggested[57] that a lubricant for use under extreme pressures may be manufactured by incorporating esterified oxidized paraffin alcohols in a high quality lubricating oil stock. The esters formed by combination of alcohols heavier than decyl alcohol with lower acids (such as mixed acetates from the oxidation of hydrocarbon wax) are particularly mentioned. MacKenzie[58] has suggested that the addition of 2 to 5 per cent of oxidized paraffin wax to a low viscosity (37 to 60 seconds Saybolt at 100° F.) oil will render it suitable for use on heavy machinery.

An oxygen polymerization product has been reported by Davis[59] which is said to improve heavy, waxy oils. This material is prepared from liquid hydrocarbons (of 10 or more carbon atoms) by low temperature oxidation treatment in the presence of a siccative. The substances formed are largely alcohols, aldehydes, ketones and esters. James[60] treats a light lubricating oil by a vapor-phase catalytic oxidation, and fractionally distils the product. The heavier ends are treated with relatively small amounts of sulphuric acid at a temperature materially above 45°C. Excess free sulphuric acid is removed, and the oil-soluble sulphonates extracted, leaving a lubricant considered to be substantially free of gum-forming constituents. The product can be used in conjunction with either engine lubricating oils or with gasoline as an overhead engine valve lubricant.

PRODUCTION OF WAXES

A partial oxidation of petrolatum can be made to yield a series of low boiling oils and a paraffin, according to Zieley.[61] The petrolatum to be treated is atomized by superheated steam and the mixture passed into a tower into which air and further superheated steam are injected at the bottom. The temperature in the reaction zone is held at about 540°C., while a pressure of 60 to 70 pounds per square inch is maintained. The condensed products of the reaction yield a paraffin and oils of oxygenated character. On the other hand it has been suggested that the oxidation products of high molecular weight hydrocarbons be heated with fats, fish oils or their derivatives. A decarboxylating catalyst is added, and the resulting condensation products are reported to be waxes suitable for polishes, sizing and impregnating agents for textiles.[62] A wax useful in preparation of shoe polishes, paper-coating materials and polishes is said to result from an esterified bleached montan wax. The bleached wax is oxidized to convert it more completely into fatty acids, and these acids are reduced to the corresponding alcohols. The resulting alcohols are then esterified with monocarboxylic acids of 10 to 25 carbon atoms, such as stearic, palmitic or linoleic acid. The physical properties (e.g., hardness) of the resulting waxy substances may be controlled by the choice of acids with which the alcohols are esterified.[63] For the production of bleached montan wax, Pungs and associates[64] suggest that the wax be first saponified and the resulting fatty acids and alcohols separated. The alcohols are bleached by a solid adsorbent, such as activated carbon, and the acids are separately treated with an oxidizing solution such as potassium bichromate and sulphuric acid. The bleached substances are then re-esterified, and by controlling the proportions of acids and alcohols used or by adding other alcohols or acids, the properties of the wax may be modified. According to Labarthe and Tressler,[65] a beeswax substitute melting at a temperature of about 75°C., or only 10° higher than the natural substance, can be made by oxidation of high-melting paraffin hydrocarbons such as "Superla" paraffin wax, melting at about 60°C. or higher, or from Utah wax (derived from Utah ozokerite). Both of these waxes are purely hydrocarbon materials, consisting almost entirely of straight- or branched-chain compounds, and have acid and ester values of practically zero. The oxidation process is carried out at a temperature between 120° and 150°C. if oxygen is used, and at a somewhat higher temperature if air is the oxidizing agent. Finely divided nickel or manganese metal or their oxides or soaps serve as catalysts in this reaction, the manganese compounds being perhaps more desirable in that they produce a lighter colored product. It is advantageous to use oxygen rather than air, since the lower temperature of the reaction under the influence of oxygen lessens decomposition of the products. Thus, in one example, 1500 g. of ozokerite wax were mixed with 15 g. of manganese oleate and maintained at 120°C. while dry oxygen was bubbled through the molten mix for 288 hours. The exhaust gases from this reaction were passed in a similar manner through a second mass of ozokerite wax and manganese oleate. At the end of the reaction time, the acid value of the first mix had risen to 25.8 and the ester value to about 50.6, while the material in the second reactor flask showed acid value of 46.7 and ester value of 56.6. The results appear to indicate, the investigators believe, that considerable proportions of high molecular weight alcohols, aldehydes and acids are formed and possibly some heavy ketones, as well.

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[57] British P. 442,921, 1935, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1936, 439.

[58] K. G. MacKenzie, U. S. P. 1,904,065, April 18, 1933, to Texas Co.; *Brit. Chem. Abs.* **B**, 1934, 135. See also, E. F. Pevere, U. S. P. 2,045,922, June 20, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 5782. B. Gallsworthy, U. S. P. 1,932,381, Oct. 24, 1933, to Texas Co.; *Brit. Chem. Abs.* **B**, 1934, 791; *Chem. Abs.*, 1934, **28**, 632.

[59] G. H. B. Davis, Canadian P. 346,032, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 2347.

[60] J. H. James, U. S. P. 2,029,619, Feb. 4, 1936, to Clarence P. Byrnes; *Chem. Abs.*, 1936, **30**, 1993.

[61] J. D. Zieley, U. S. P. 1,944,483, Jan. 23, 1934, to Amarel Corp.; *Brit. Chem. Abs.* **B**, 1934, 1001; *Chem. Abs.*, 1934, **28**, 2177.

[62] French P. 45,129, 1935 (addition to French P. 759,261), to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 2670.

Oxidized waxes have been suggested as substances useful in improving the adhesive properties of road bitumen, particularly in the presence of water. The addition of 0.1 to 2 per cent of oxidized paraffin wax materials is said to make bituminous road oils hold the aggregate materials more firmly.[66] Oxidized montan or carnauba wax is capable of acting as a vehicle or adherent in preparing wax-impregnated ceramics or wax-coated metallic vessels, according to Sommer, Weissbach and Reinhardt.[67] The waxy products obtained by the oxidation of montan wax are mixed with paraffin, ceresin or ozokerite wax and applied to the stock to be treated. The resultant walls are reported to be impervious to acids.

MISCELLANEOUS OXIDATION PRODUCTS

Resins. Industrially useful resins may be prepared by the oxidation of petroleum fractions, or by treatment of the oxidation products obtained from petroleum fractions.[68] Thus, treatment of a gasoline fraction with air or oxygen may furnish a synthetic resin, Borst[69] reports. In the process he proposed, a Mid-Continent residuum was pyrolyzed to yield a cracked gasoline boiling between 40° and 220°C. This material was placed in a pressure vessel provided with an inlet spray line. The vessel was heated to approximately 150°C. and a mixture of about equal parts of air and oxygen was introduced until about 3 pounds of gummy material was produced per gallon of original gasoline. The pressure apparatus was then cooled and opened. The remaining hydrocarbon was decanted, and a heavy metal oxide (15 per cent by weight of ferric oxide) was added, the bomb was closed and the mixture subjected to further oxidation under substantially the same conditions as in the first stage.

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[63] W. Pungs and M. Jahrstorfer, U. S. P. 1,942,833, Jan. 9, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1824.

[64] W. Pungs, M. Jahrstorfer and T. Hellthaler, U. S. P. 1,985,871, Dec. 25, 1934, to A. Riebeck'sche Montanwerke A.-G.; *Brit. Chem. Abs.* **B**, 1935, 1127; *Chem. Abs.*, 1935, **29**, 1233.

[65] J. Labarthe and D. K. Tressler, U. S. P. 1,983,672, Dec. 11, 1934, to Mathieson Alkali Works, Inc.; *Brit. Chem. Abs.* **B**, 1935, 1127; *Chem. Abs.*, 1935, **29**, 859.

[66] British P. 429,548, 1934, to N. V. de Bataafsche Petroleum Maatschappij; *Chem. Abs*, 1935, **29**, 7610; *Brit. Chem. Abs.* **B**, 1935, 758.

[67] W. Sommer, H. Weissbach and L. Reinhardt, German P. 609,162, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 3074; *J. Inst. Pet. Tech.*, 1935, **21**, 269A.

After this treatment, the resinous material was drawn off hot, mixed with an equal weight of wood flour and about two per cent of hexamethylenetetramine (calculated on total weight of resin and filler) was added. The resulting mass was worked on hot rolls at about 175°C., and the final resin pulverized to yield a powder capable of hot molding. Morrell[70] suggests an analogous treatment using ozonized air as the oxidizing agent in place of the air-oxygen mixture.

The large variety of useful materials obtained by oxidation treatment is indicated by a report of Velikovskaya[71] on the utilization of by-products of the petroleum industry. From the acid sludge produced in spindle oil refining, he reports, a satisfactory axle grease can be made. The acid sludge is heated to 300°C. and blown with air till it solidifies. The product is then heated to 170°C. and diluted with mineral oil to the desired viscosity and finally treated with 1 per cent of 35° Baumé sodium hydroxide. A shoemaker's wax can be prepared from heavy oil bottoms stripped of fractions boiling below 300°C. and similarly blown with air until solidification sets in. This product is then mixed with 20 per cent of heavy distillate alkali sludge or with oil separated from acid sludge after it has been blown with air. A binder material from the manufacture of briquets can also be prepared from acid sludge.

Insecticides. Investigations by Francis[72] on the efficiency of insecticides indicated that although the exposed feeders, such as caterpillars, hoppers, beetles and bugs, are best controlled by applications of poisons on the feeding materials and contact insecticides, the concealed feeders such as leaf miners, borer and ants are most readily attacked by gases and a number of petroleum preparations. The sucking insects are most difficult to control, since the feeding materials cannot be poisoned. For this type of pest, substances which affect respiration or have a caustic effect on the skin are used; insect powders, tobacco, and petroleum distillates. Household moths are eradicated by suffocants; carbon disulphide, hydrogen cyanide or volatile petroleum products. It was shown in tests carried out at the New Jersey Agricultural Experiment Station that insects normally have a coating which is highly resistant to the penetration of water. Petroleum distillates overcome this natural protection. The lighter oils have, *per se*, a caustic action on the softer parts of the insect's body. According to Petrov,[73] the paraffin base oils are best suited to the preparation of insecticides, and the naphthenic oils are distinctly inferior. A number of Russian oils were tested as insecticide preparations, and it was found that this general comparison holds. Aromatic content is particularly undesirable in insecticide oils due to the burning action it evidences when applied to plant foliage.[74] Hyman[75] has prepared an insecticide by oxidation of a vapor-phase cracked petroleum distillate boiling in the kerosene to gas-oil range. The cracked product is treated with molecular oxygen in the presence of a siccative soap or other siccative compound of cobalt, lead or manganese. When precipitation ceases, the solid is separated out and the filtrate recovered. It has also been suggested that the sodium salts of the saturated aliphatic acids of medium molecular weight (4 to 15 carbon atoms) make effective insecticides. These can be prepared, Burwell[76] states, by the oxidation of petroleum fractions. The hydrocarbon is oxidized (with oxygen or air) under pressure of 250 pounds per square inch in the presence of manganese oleate at a temperature of 155°C. The product is said to be useful as a constituent of insecticidal sprays.

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[68] See Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935. See also Chapter 38.

[69] W. B. Borst, U. S. P. 2,066,090, Dec. 29, 1936, to Universal Oil Products Co.; *Chem. Abs.*, 1937, **31**, 1119.

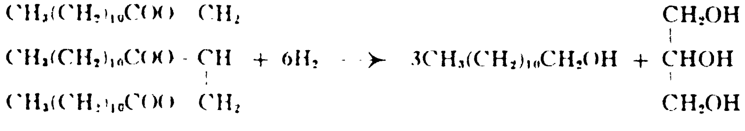
[70] J. C. Morrell, U. S. P. 2,066,120, Dec. 29, 1936, to Universal Oil Products Co.

[71] E. Velikovskaya, *Neft*, 1933, **4**, No. 10, 14; *Brit. Chem. Abs.* **B**, 1935, 885; *Chem. Abs.*, 1935, **29**, 1971.

[72] C. K. Francis, *Oil Gas J.*, 1934, **32** (33), 16; *J. Inst. Pet. Tech.*, 1934, **20**, 261A; *Chem. Abs.*, 1934, **28**, 2108.

[73] A. D. Petrov, *Bull. Plant Protection (U.S.S.R.)*, 1931, **3**, No. 1, 189; *Chem. Abs.*, 1933, **27**, 5876; *J. Inst. Pet. Tech.*, 1934, **20**, 382A. *Foreign Pet. Tech.*, 1933, 1 (2), 40.

Derivatives of the higher alcohols have been tested as contact insecticides, according to Bousquet, Salzberg and Dietz,[77] and the results obtained have been encouraging. These higher alcohols can be obtained by the oxidation of the higher petroleum derivatives, though in the present investigation they were derived from cocoanut oil and transformed to the rhodanates for the insecticide tests. The following series of reactions was employed, starting with trilaurin:



$$\begin{array}{l} CH_3(CH_2)_{10}COO-CH_2 \\ \qquad\qquad\qquad\quad | \\ CH_3(CH_2)_{10}COO-CH \\ \qquad\qquad\qquad\quad | \\ CH_3(CH_2)_{10}COO-CH_2 \end{array} + 6H_2 \longrightarrow 3CH_3(CH_2)_{10}CH_2OH + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

$$CH_3(CH_2)_{10}CH_2OH + HCl \longrightarrow CH_3(CH_2)_{10}CH_2Cl + H_2O$$
$$CH_3(CH_2)_{10}CH_2Cl + NaSCN \longrightarrow CH_3(CH_2)_{10}CH_2SCN + NaCl$$

By starting with cocoanut oil, it is possible in this way to obtain the rhodanates of all the even-numbered carbon atom alcohols from six to eighteen carbon atoms. These include hexyl, octyl, decyl, lauryl, myristyl, cetyl and stearyl rhodanates. Hexyl rhodanate is an oily liquid boiling at 85°C. whereas stearyl rhodanate is a waxy solid boiling at 195°C. under 2 mm. pressure. The lower rhodanates have powerful and unpleasant odors whereas the longer chain compounds are much less objectionable. Lauryl rhodanate has a mild and fatty odor.

A series of tests made against several varieties of aphids, red spiders and thrips showed that the 12 carbon (lauryl) rhodanate was uniformly the most effective. In several instances it was found that the lowest rhodanates tested (methyl, ethyl and butyl) were positively advantageous to the insects, since potassium oleate, the wetting agent employed in conjunction with the insecticides, was more toxic alone than the combination of oleate and butyl rhodanate. There was a sharp increase in toxicity with hexyl rhodanate, a further distinct increase for octyl rhodanate, and a lesser gain, and in some cases (as against the green chrysanthemum aphid) little or no gain in going to the decyl rhodanate. The curve of toxicity flattens between the decyl and lauryl rhodanates, thence declining rapidly for myristyl, cetyl and the higher compounds. (See Figs. 252 and 253.) It was found in testing various concentrations that lauryl rhodanate in 0.067 per cent concentration caused practically a 100 per cent kill of green chrysanthemum aphids. Since this 12-carbon rhodanate showed greatest promise, it was tested in some detail as to plant toxicity and is reported to allow a sufficient margin of safety for effective use as a practicable insecticide.

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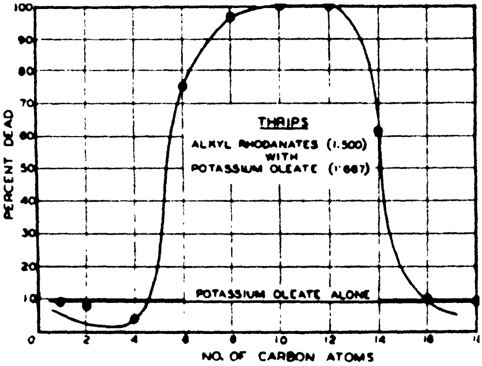
[74] See also R. P. Tucker, *Ind. Eng. Chem.*, 1936, **28**, 458; *Chem. Abs.*, 1936, **30**, 3575; *J. Inst. Pet. Tech.*, 1936, **22**, 272A. See Chapter 51.

[75] J. Hyman, U. S. P. 2,020,648, Nov. 12, 1935, to Velsicol Corp.; *Chem. Abs.*, 1936, **30**, 566.

[76] A. W. Burwell, British P. 429,185, 1935, to Alox Chem. Corp.; *J. Inst. Pet. Tech.*, 1935, **21**, 313A; *Chem. Abs.*, 1935, **29**, 7006.

[77] F. W. Bousquet, P. L. Salzberg and H. F. Dietz, *Ind. Eng. Chem.*, 1935, **27**, 1342; *Chem. Abs.*, 1936, **30**, 223; *Brit. Chem. Abs.* **B**, 1936, 117; see also P. L. Salzberg and E. W. Bousquet, U. S. P. 1,963,100, June 19, 1934, to Grasselli Chem. Co.; *Chem. Abs.*, 1934, **28**, 4749; *Brit. Chem. Abs.* **B**, 1935, 348 and U. S. P. 1,993,040, March 5, 1935, to Grasselli Chem. Co.; *Chem. Abs.*, 1935, **29**, 2656; *Brit. Chem. Abs.* **B**, 1936, 387.

James[78] suggests that the mixed oxidation products of a gas oil may be treated with sulphuric acid or oleum, producing sulphates and sulphonates of the unsaturated compounds present. By neutralization of the acid mixture, hydrolysis of the sulphates occurs, yielding higher alcohols, which, he states, may be combined with a toxic agent to produce an insecticide. If the neutralization is effected by the addition of sodium sulphide to the acid liquors, the sulphur content of the product is reported to be about 2.5 per cent. The sulphur has in part, he finds, reacted to form thio ethers, which act as a toxic agent to the insects, without injuriously affecting foliage. Chlorine or nitrogen compounds may be introduced into the organic molecule instead of sulphur.



Courtesy Industrial and Engineering Chemistry

FIG. 252.—Relative Efficiency of Alkyl Rhodanates in Killing Thrips. (E. W. Bousquet, P. L. Salzberg and H. F. Dietz)

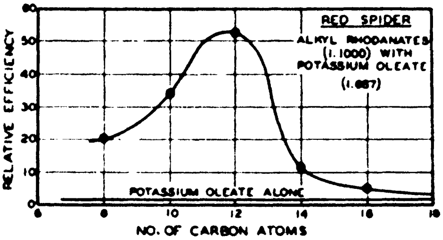
Emulsifying Agents. The acids and esters of oxidized petroleum fractions have considerable emulsifying powers, and their cheapness makes them desirable in many processes. Eigeles[79] has reported tests made on the flotation of Kalanguev fluorite ore, using oxidized paraffin and the mixed carboxylic acids separated from it. In this service it was found that the best solvent for the oxidized paraffin was benzene, although the carboxylic acids gave satisfactory results with kerosene. Up to 16 per cent of the oxidized paraffin solution can be used, and solutions containing 30 per cent of the carboxylic acids were tested. It was reported that these solutions were less sensitive to variations of the pH values than were oleic acid flotation solutions. However, an optimum result was obtained at pH of 11. The best temperatures for the operation varied somewhat, that for the oxidized paraffin being 23° to 24°C., although the carboxylic acids gave good results at 12°C. The addition of pine oil improves the flotation by petroleum oxidation products, although the regular procedure used in the oleic acid flotation gives equally good results (*e.g.*, 81.4 per cent of the calcium fluoride present in the ore

[78] J. H. James, U. S. P. 2,067,532, Jan. 12, 1937, to C. P. Byrnes.

[79] M. A. Eigeles, *Mineral Suir'e*, 1934, **9**, No. 6, 44; *Chem. Abs.*, 1934, **28**, 6951.

before treatment was extracted into the flotation concentrate. The concentrate analyzed 96 per cent fluorite.) when the oxidized paraffin is simply substituted.

Some of the oxidized petroleum compounds also have the power to break emulsions of the water-in-oil type. Thus Burwell[80] oxidized petroleum oil hydrocarbon at 155°C. under a pressure of 350 pounds per square inch in the presence of manganese oleate. The ketonic fraction of the product or the mixed acids or their sulphonation products may be employed in breaking petroleum emulsions. Similarly, sulphonated oxidized products of higher petroleum hydrocarbons can be used as wetting and dispersing agents in making oil-in-water emulsions.[81]



Courtesy Industrial and Engineering Chemistry

FIG. 253.—Comparison of Insecticidal Action of Alkyl Rhodanates Against Red Spider. (E. W. Bousquet, P. L. Salzberg and H. F. Dietz)

SPECIAL METHODS OF COMBUSTION

A special case of partial oxidation of hydrocarbon oils has been suggested by Janssen,[82] using a slurry of oil and metal ore. Oil and finely divided ore are thoroughly mixed, and air is blown through the mixture in the presence of a catalyst to produce fatty acids. Alkali is added to the mixture so produced to form soaps. The fuel slurry is then atomized and burned with such a quantity of air that incomplete combustion takes place and the metal ore is reduced.

In an effort to secure greater fuel efficiency, submerged combustion has been studied from time to time. Thus, according to Kobe,[83] one type of commercial submerged combustion burner, consuming hydrocarbon gas and air, will utilize the latent heat of volatilization of the water produced by the combustion since the products of combustion are cooled to the temperature of the liquid being heated. The burners are capable of converting over 90 per cent of the available energy of the fuel-air mixture into useful heat, this investigator indicated. Kobe, Conrad and Jackson[84] reported experiments with submerged combustion burners and found that three essential considerations in the construction of such a mechanism were: (a) a mixing chamber which would produce a homogeneous air-gas mixture, (b) a velocity tube through which the air-gas mixture flows at a rate greater than the rate of flame propagation in the mixture, and (c) a combustion chamber containing a refractory surface which becomes incandescent and acts as an ignition point for the fuel mixture. With an experimental burner constructed according to these observations, the thermal efficiency in evaporation of water (percentage of heat input recovered in products) was 95.2 per cent, while 83.6 per cent of the heat input was used in evaporating the water. The investigators tried submerged combustion evaporation in the concentration of sulphite waste liquors. The most serious problems in the evaporation of these liquors are the viscosity of the fluids, the serious scale-forming tendencies, the corrosive nature of the unneutralized liquid, foaming, and the escape of volatile substances causing trouble in condensing. Submerged combustion makes possible the use of poor heat-conducting materials such as ceramic ware which resist corrosion, while scale does not interfere with heat transfer from a gas bubble. The continuous release of gases tended to agitate the material satisfactorily, and good concentration results were reported. Since these experiments, Kobe, Hague and Carlson[85] have studied the dehydration of sodium sulphate decahydrate by submerged combustion. The dehydration of this salt is difficult because of the peculiar solubility curve of the compound. At 32.4°C. this salt forms solid sodium sulphate and a saturated solution. Evaporation must be conducted below this temperature, then, if scale deposition is to be avoided, or the evaporation process must start with a saturated solution rather than the decahydrate itself. With tube evaporators, there must be considerable surface at a temperature higher than that of the liquid, with consequent deposition of the anhydrous salt on these surfaces and lowered efficiency resulting from poor heat transmission. On the other hand, submerged combustion is said to be highly advantageous in that no large metal surfaces are exposed at temperatures higher than that of the liquid. Some scale does form on the burner, but the unit need not be shut down; the burner is withdrawn, another burner being inserted. When submerged combustion is employed, solid decahydrate may be used as the feed material, reducing the required evaporation. Further, the inverted solubility curve

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[80] A. W. Burwell, U. S. P. 1,993,646, March 5, 1935, to Alox Chem. Corp.; *Brit. Chem. Abs.*, B, 1936, 438; *Chem. Abs.*, 1935, **29**, 2730.

[81] German P. 608,362, 1935, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech.*, 1935, **21**, 224A; *Chem. Abs.*, 1935, **29**, 2626. See also E. A. Mauersberger, French P. 801,106, 1936; *Chem. Abs.*, 1937, **31**, 184.

[82] H. J. Janssen, Canadian P. 354,308, 1935, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 1728.

[83] K. A. Kobe, *Chem. and Met.*, 1934, **41**, 300; *Chem. Abs.*, 1934, **28**, 4804; *Brit. Chem. Abs.*, B, 1934, 735.

[84] K. A. Kobe, F. H. Conrad and E. W. Jackson, *Ind. Eng. Chem.*, 1933, **25**, 984; *Chem. Abs.*, 1933, **27**, 5123; *Brit. Chem. Abs.* B, 1933, 944.

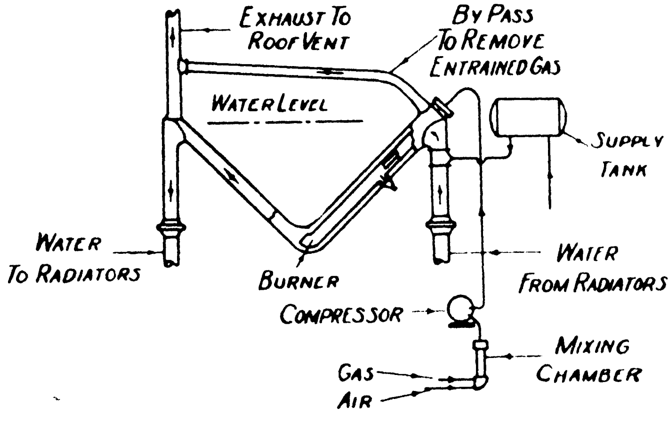

FIG. 254.—Sketch of Submerged Combustion Heater for Domestic Use. (R. M. Stewart)

of the salt permits recovery of a considerable portion of the material as the anhydrous salt by the solubility effect without evaporating water. Analogous investigations on the recovery of potassium chloride from sylvanite solutions showed equally promising results.[86]

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[85] K. A. Kobe, C. W. Hague and C. J. Carlson, *Ind. Eng. Chem.*, 1936, **28**, 589; *Chem. Abs.*, 1936, **30**, 3949.

Stewart[87] has pointed out a further advantage of submerged combustion as a source of heat; it makes possible an extremely compact boiler-burner unit. For instance, he has made an apparatus for domestic heating consisting of an angled pipe enclosing a tubular burner. The annular space between the inner burner tube and the external pipe contains the water of the boiler system. (See Fig. 254.) Air-fuel mixture is supplied to the burner by a small compressor. If used in conjunction with a domestic hot-water heating system, the burner is preferably placed at the top of the house, in order that the water-head on the burner may be minimized. Circulation in this system is not dependent on convection currents, since the combustion gases forced from the burner serve to maintain a rapid circulation through the burner-boiler unit and hence through the entire system. The intimate contact of combustion products and water makes heat transfer highly efficient (over 90 per cent), it is said. The small size of the apparatus required makes practicable the use of corrosion-resistant materials without undue increase in cost. Further, because the gases are fed by means of a small blower, and the combustion products leave the system at a temperature below the boiling point of water, a chimney or flue is unnecessary, since high temperature gases need not be handled, and draft is otherwise supplied. The exhaust flue may be a 1-inch malleable iron pipe. This type of apparatus is not limited to direct heating, however, since the burner-boiler unit is sufficiently compact to be immersed directly in a fluid which is to be heated without contact with the combustion gases.

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[86] K. A. Kobe and R. P. Graham, *Ind. Eng. Chem.*, 1936, **28**, 593.

[87] R. M. Stewart, U. S. P. 2,025,695, Dec. 24, 1935, to Ellis-Foster Co.

Chapter 46

Sulphonation of Petroleum Hydrocarbons. Sulphonic Acids, Detergents and Other Products

In view of the large-scale application of acid refining of petroleum distillates, the action of sulphuric acid and of oleum on various fractions is of importance. In addition to its action as a solvent and precipitating or coagulating agent, the acid effects sulphonation, polymerization and sulphation of petroleum hydrocarbons. In many instances, some oxidation also occurs simultaneously. A consideration of the solvent or precipitating action of the acid involves a discussion of petroleum refining which is beyond the scope of this text. The sulphation and polymerization which take place with olefins has been described previously.[1] In this chapter attention is directed particularly to sulphonation, especially of paraffin hydrocarbons.

The early use of sulphuric acid in petroleum refining[2] soon led to the serious problem of disposal of the acid sludge, a highly corrosive substance,[3] which, however, contained considerable amounts of valuable constituents. The sludge was diluted with water, causing a separation into two layers. The aqueous layer was reconcentrated and the sulphuric acid re-used; the insoluble oily residue was burned as a fuel.[4]

As uses have developed for the substances present in the acid sludge, many workers have investigated methods of separation applicable to such complex mixtures. The characteristics of sludges depend on the properties of the original crude, the fraction treated, and the method of treatment. The latter varies in severity from the mild processes employed in refining light gasoline distillates, through the more severe treatment of lubricating oils to the rigorous operations necessary in the manufacture of white oils and petrolatum where the most concentrated acid, and frequently fuming oleum, is used.[5]

PROPERTIES OF SULPHONIC ACIDS

Since accurate knowledge of the mechanism of sulphonation is limited to the reaction of hydrocarbons of relatively low molecular weight, only inferences can be drawn regarding the reactions of the larger molecules present in petroleums. It appears that the saturated hydrocarbons in the higher distillates of many oils are much more reactive toward chemical reagents, sulphuric acid included, than are the simpler saturated compounds, while the almost unknown class of polynuclear cycloparaffins may embrace more highly reactive constituents than has been suspected.

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[1] See Chapters 13, 14 and 15 for sulphation, and Chapter 26 for polymerization.

[2] For more details of earlier work see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[3] For a discussion of this, see K. P. Likhushin, *Neft. Khoz.*, **1934**, No. 9, 87; *Chem. Abs.*, 1935, **29**, 6032; *Brit. Chem. Abs.* **B**, 1936, 627.

[4] A modification of this process, using water and a substantial proportion of a spacing agent such as a sulphate or sulphonate has been described by J. C. Morrell (U. S. P. 1.930.249, Oct. 10, 1933, to Universal Oil Products Co.; *Chem. Abs.* 1934, **28**, 312). Settling separates the sludge into an oily layer and an aqueous layer; fresh acid is added to the aqueous layer.

[5] See for example A. Lazar, U. S. P. 1,964,953, July 3, 1934, to Associated Oil Co.; *Brit. Chem. Abs.* **B**, 1935, 1023; *Chem. Abs.*, 1934, **28**, 5181. Also K. T. Steik, *Am. Dyestuff Reptr.*, 1934, **24**, 480; *Chem. Abs.*, 1935, **29**, 6766; *Brit. Chem. Abs.* **B**, 1935, 989, and B. K. Tarasov, *Neft. Khoz.*, **1929**, No. 16, 236; *Chem. Abs.*, 1929, **23**, 4812.

As the chemical and physical properties of acid sludges are dependent on a number of factors, investigations of these complex mixtures have been difficult and many procedures have been advocated for separation of the sulphonic acids therefrom. The latter in turn may be subdivided in two ways, according to their solubility, or that of their calcium salts in various solvents. Thus the so-called "mahogany acids" are oil-soluble and the "green acids" are water-soluble. The calcium salts resulting from neutralization of acid sludge by calcium carbonate (or hydroxide) can be separated into three classes, the α-, β- and γ-sulphonates as follows:[6]

α-Sulphonates: Found mainly in the acid sludge, but also in the oil layer. The calcium salts are insoluble in water and ether.

β-Sulphonates: Found largely in the oil phase, but also occur in the sludge when oleum is used. Calcium salts are insoluble in water, but soluble in ether.

γ-Sulphonates: Found almost entirely in the acid sludge. The calcium salts are soluble in water, insoluble in ether.

Taking advantage of this means of separation, von Pilat and Szankowski[7] extracted γ-calcium sulphonates obtained by sulphonation of a transformer oil and regenerated the hydrocarbons from them. The oils so secured gave evidence that these γ-acids were derived from a homologous series of aromatic hydrocarbons (without long side-chains), the heavier fractions showing indications of condensed ring-systems. The ratio of carbon to hydrogen atoms in the molecule (about one to one) holds even with increasing molecular weight. The oils are characterized by high refractive indices, a very steep temperature-viscosity curve and a density about unity.

Sereda[8] has reported a specific test for the β-sulphonic acids that is said to be unaffected by the presence of naphthenic or polysulphonic acids. Ferric salts react with the β-acids to form a compound intensely blue in ether solution. The color is not given by either the α- or the γ-acids, and when conducted with a *p*H value between 2 and 9, the response is discernible in concentrations as low as one part in 5000.

A separation[9] of mixed naphthenic and sulphonic acids and petroleum oils can be brought about by treating a dilute aqueous solution of the neutralized salts with ether to remove free oils, followed by a cold brine solution. The sulphonic salts react with the brine to form water-soluble sodium salts, while the naphthenic acids do not. The latter may then be extracted with a light petroleum. It is reported that a determination made in this way is accurate to 0.2 to 1 per cent (determined on total original mixture).

Investigating α- and γ-sulphonic acids, Neyman and von Pilat[10] determined the surface-tension effects of the sodium salts and showed these substances to be much more effective in decreasing surface tension of water than was sodium oleate.

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[6] S. von Pilat, J. Sereda and W. Szankowski, *Petroleum Z.*, 1933, **29** (3), 1; *Chem. Abs.*, 1933, **27**, 2287; *Brit. Chem. Abs.* **B**, 1933, 211. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[7] S. von Pilat and W. Szankowski, *Petroleum Z.*, 1935, **31**, 1; *Brit. Chem. Abs.* **B**, 1935, 438; *Chem. Abs.*, 1935, **29**, 7057.

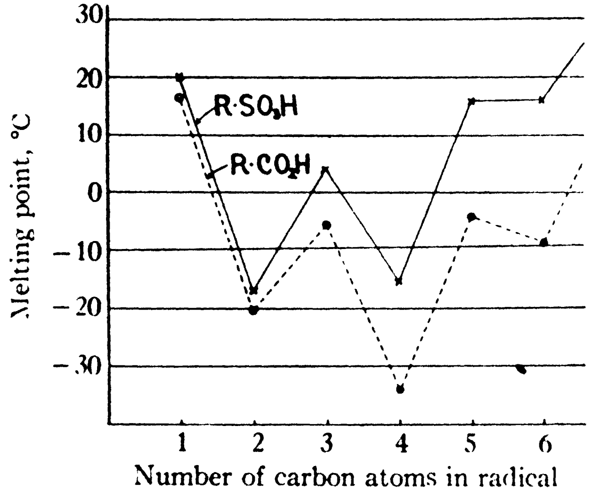
[8] J. Sereda, *Petroleum Z.*, 1934, **30**, No. 19, 1; *Chem. Abs.*; 1934, **28**, 4872; *Brit. Chem. Abs.* **B**, 1934, 612.

[9] S. von Pilat and J. Sereda, *Fettchem. Umschau*, 1934, **41**, 171, 200, 237; *Brit. Chem. Abs.* **B**, 1935, 132; *Chem. Abs.*, 1935, **29**, 2702.

[10] E. N. Neyman and S. von Pilat, *Ind. Eng. Chem.*, 1934, **26**, 395; *Chem. Abs.*, 1934, **28**, 4577; *Brit. Chem. Abs.* B, 1934, 486. According to these investigators α- and γ-sulphonic acids constitute about 25 to 40 per cent of the bulk of the acid sludge obtained from treatment of lubricating oils with concentrated sulphuric acid. See *Ind. Eng. Chem.*, 1934, **26**, 651.

The surface tensions of 0.1 per cent solutions of the sodium salts of oleic, α- and γ-acids were 65, 51 and 54 dynes per square centimeter, respectively. Dialysis using a triple collodion membrane permitted complete separation of the γ-sulphonate from the larger molecules of the α-salt, and by analysis it was determined that the γ-salt contains about 31 atoms and the α-salt twice that number. Solutions of 0.01 per cent strength showed only a feeble Tyndall effect under the ultramicroscope, and no Brownian motion.

Vivian and Reid[11] prepared some of the lower alkyl sulphonic[12] acids by oxidation of corresponding mercaptans and dehydration, at one millimeter pressure, of the resulting concentrated aqueous solutions. The acids appeared unstable and soon darkened even when stored *in vacuo*. Investigations of the melting points of the alkyl sulphonic acids containing from 1 to 6 carbon atoms showed an alternation of melting points closely paralleling those of the corresponding carboxylic acids. (See Fig. 255.) Reed and Tartar[13] investigated the aqueous solutions of the calcium, magnesium and sodium salts (prepared by the Strecker reaction[14]) of the higher alkylsulphonic acids through octyl, decyl, lauryl, myristyl, cetyl and *n*-octadecyl. Investigations of surface tension showed a considerable time-function, and the capillary rise method was recommended for studying this property. Considerable time (more than a month) was required before these capillary surface tension values reached equilibrium. Similar time effects were found in measuring the interfacial tension of the aqueous solution against benzene, though the factor



Courtesy Journal of American Chemical Society

FIG. 255.—Melting Points of Sulphonic and Carboxylic Acids. (D. L. Vivian and E. E. Reid)

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[11] D. L. Vivian and E. E. Reid, *J.A.C.S.*, 1935, **57**, 2559; *Chem. Abs.*, 1936, **30**, 1741; *Brit. Chem. Abs.* **A**, 1936, 312.

[12] For the industrial preparation of higher alkyl sulphonic acids, see L. Szegö and G. de Ponte, *Atti congr. naz. chim. pura applicata, 5th Congr.*, 1936, **14**, 870; *Brit. Chem. Abs.* **B**, 1937, 415.

[13] R. M. Reed and H. V. Tartar, *J.A.C.S.*, 1935, **57**, 570; *Chem. Abs.*, 1935, **29**, 2915; *Brit. Chem. Abs.* **A**, 1935, 606; *J.A.C.S.*, 1936, **58**, 322; *Chem. Abs.*, 1936, **30**, 2465; *Brit. Chem. Abs.* **A**, 1936, 421.

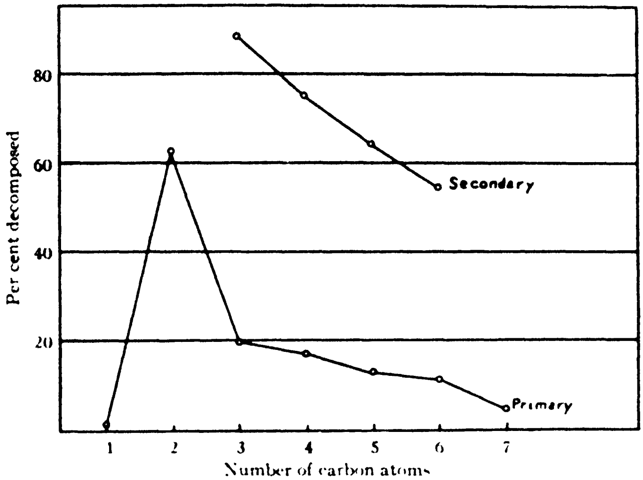
[14] For a general discussion of this reaction see Chapter 34. In this case the reaction used was:

$$RI + (NH_4)_2SO_3 \longrightarrow RSO_3NH_4 + NH_4I$$

in this case was measured in weeks rather than months. Conductivity experiments demonstrated that the sodium alkyl sulphonates are similar in this respect to potassium fatty acid soaps.

Although the sulphonic acids react as strong acids, Dominikiewicz[15] reports that amphoteric elements such as aluminum form two types of salts, a true aluminum sulphonate and a second type of salt in which the aluminum atom is a part of the aluminosulphonic acid ion.[16]

The stability of aliphatic sulphonic acids, probably because of the carbon-sulphur linkage, is shown by the fact that they are not hydrolyzed by aqueous alkali except when heated to temperatures of 315 to 375°C.[17] Under such conditions three reactions are possible, viz.:



Courtesy Journal of American Chemical Society

FIG. 256.—Decomposition of Aliphatic Sulphonic Acids with 3.70 N Sodium Hydroxide. 3 Hours at 345°C. (F. C. Wagner and E. E. Reid)

$$RCH_2CH_2SO_3Na + NaOH \longrightarrow RCH{=}CH_2 + Na_2SO_3 + H_2O$$
$$RCH_2CH_2SO_3Na + NaOH \longrightarrow RCH_2CH_3 + Na_2SO_4$$
$$RCH_2CH_2SO_3Na + NaOH \longrightarrow RCH_2CH_2OH + Na_2SO_3$$

Although no alcohols have been isolated as a result of such reactions, nevertheless in some instances it was reported that the hydrolytic products contained alkali salts of carboxylic acids having the same number of carbon atoms as the initial sulphonic acid. For example, *n*-butyl and *n*-amyl sulphonic acids yielded butyric and valeric acids, respectively. This appeared to indicate that the third reaction (given above) was the main one, followed by interaction of the liberated alcohol and alkali at high temperatures.

$$RCH_2CH_2OH + NaOH \longrightarrow RCH_2COONa + 2H_2$$

Comparisons of percentage decompositions of various aliphatic sulphonic acids, with 3.70 N sodium hydroxide for 3 hours at 345°C., indicated methyl sulphonic to be the most, and ethyl sulphonic the least, stable. The stability of acids having higher molecular weights then increased with the number of carbon atoms per molecule. This is shown graphically in Fig. 256. In general, sulphonic acids derived from secondary hydrocarbons were less stable than those from primary hydrocarbons. The effect of temperature (when the same concentration of alkali and the same heating time mentioned above were employed) is illustrated in Fig. 257. It will be noted that for the same percentage decomposition much higher temperatures are required in the case of primary sulphonic acids than for the corresponding secondary compounds.

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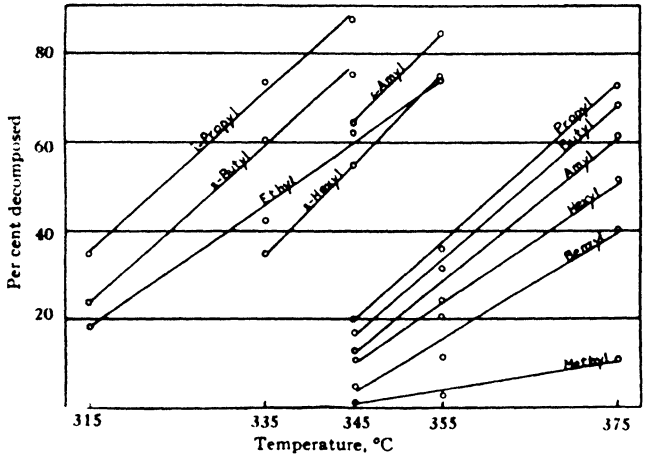
[15] M. Dominikiewicz, *Arch. Chem. Farm.*, 1934, **1**, 93; *Chem. Abs.*, 1935, **29**, 5429; *Brit. Chem. Abs.* **A**, 1934, 889.

[16] For a general review of the properties of the sulphonic acids derived from petroleum, see, C. F. Nabuco de Araujo, Jr., *Rev. chim. ind.* (*Rio de Janeiro*), 1934, **3**, 218; *Chem. Abs.*, 1934, **28**, 6987.

[17] F. C. Wagner and E. E. Reid, *J.A.C.S.*, 1931, **53**, 3407; *Chem. Abs.*, 1931, **25**, 5393; *Brit. Chem. Abs.* **A**, 1931, 1268.



Courtesy Journal of American Chemical Society

FIG. 257.—Effect of Temperature on Decomposition of Aliphatic Sulphonic Acids with 3.70 N Sodium Hydroxide. (F. C. Wagner and E. E. Reid)

However, despite the strong resistance of sulphonic acids to hydrolysis (even in the presence of caustic alkali), Sereda, Macura and Udrycki[18] report that the interaction of these acids and organic bases such as aniline results in splitting of the carbon-sulphur bond comparatively readily. Up to about 160°C., the reaction between aniline and sulphonic acids yields the expected anilides. When the two reactants are heated above this temperature, the products are chiefly sulphanilic acid and a hydrocarbon.

$$RSO_3H + C_6H_5NH_2 \longrightarrow H_2NC_6H_4SO_3H + RH$$

The reaction followed the same course with *o*-toluidine, yielding 3,4-methylaminobenzenesulphonic acid. However, *p*-toluidine did not effect the removal of the sulphonic group even on prolonged boiling, reaction beginning at 230°C. under pressure. When dry *p*-toluidine was heated with absolutely anhydrous sulphonic acids at this temperature, 5,2-methylaminobenzenesulphonic acid was formed. From these reactions it was believed that when the position para to the amino group is occupied, the sulphonic group is directed to the ortho position.

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[18] J. Sereda, K. Macura and A. Udrycki, *Ber.*, 1935, **68**, 1933; *Chem. Abs.*, 1936, **30**, 442; *Brit. Chem. Abs.* **B**, 1935, 1081.

PRODUCTION OF SULPHONIC ACIDS

Parkhomenko[19] reports that for best results both the oil and the oleum employed should be of uniform quality. He recommends that 18 to 20 per cent of oleum (23 to 25 per cent free sulphur trioxide) be used in four treatments of two and a half hours, the temperature being maintained at 75 to 80°C. The use of air for agitating the reactants is not advisable. In separating the acids produced, a thorough settling is necessary, and he recommends that two settlings in separate vessels be made, at a temperature of 45 to 50°C. By these methods, he found a sulphonic acid-oil ratio of 2:1 in the first two extractions and about 4:3 in the last two. Voznesenskii[20] treated a distillate (initial boiling point 220°C., 85 per cent over below 240°C.) with 20 per cent oleum four successive times, and a yield of nearly 40 per cent of sulphonic acids was obtained. These acids were found to be effective fat-hydrolyzing agents, although the sulphonic acids obtained from liquid petrolatum were 120 per cent better in this respect. Khisin and Sungalovskaya[21] report sulphonating a heavy fraction (boiling between 275 and 350°C.) of a Gdov shale-oil tar to make effective soaps. The oil was treated with 150 per cent of its volume of sulphuric acid for one hour at 60°C. A yield of 60 per cent of sulphonic acids was reported, and the sodium or ammonium salts of these acids were found to be serviceable soaps.

Sulphur trioxide in gaseous form may be employed as the sulphonating agent, and according to Sarkisov, Gotovtzev and Razderishin,[22] this method is advantageous in that it makes possible a higher concentration of sulphonic acids in the crude products. By using gaseous sulphur trioxide and dry air blown through oil at a temperature of 110 to 120°C. the sulphonic acid concentration was increased 15 per cent, while the free sulphuric acid concentration in the solution was held to a minimum. Some investigations by Likhushin, Dei-Karkhanova and Shaknovich,[23] in which various petroleum distillates were treated with sulphur trioxide, led them to the conclusion that petroleum sulphonic acids were not formed from naphthenic acids, but from naphthenic hydrocarbons that had suffered dehydrogenation. Shneider and Kheifetz[24] reported, however, that in treating a gas oil with sulphur trioxide, they were able to increase the yield of sulphonic acids by 50 per cent when 4 per cent of naphthenic acids were added. This observation was confirmed by Likhushin, Dei-Karkhanova and Mirzakulieva.[25] The latter investigators treated distillates (at 60 to 63°C.) with 4 portions of sulphur trioxide (a total of 12 per cent being used). Very high yields of acids were obtained, and it was concluded that there was either a catalytic action caused by the naphthenic acids present, or that the naphthenic acids had a dissolving action on the sulphonic acids in the distillates.

Such powerful sulphonating agents as sulphur trioxide are seldom used in usual refining operations, but the trioxide may be modified to yield a maximum proportion of sulphonic acids with a minimum of oxidation, using sulphuric acid as the refining agent. The best conditions for such results are 10 per cent (by weight) of 96 per cent sulphuric acid at −10°C. Less concentrated acid (90 per cent) can be used at a higher temperature (+15°C.) if a larger proportion (20 per cent) is employed.[26]

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[19] V. Parkhomenko. *Neft*, 1932, **3**, No. 3-4, 30; *Chem. Abs.*, 1935, **29**, 2702.

[20] A. A. Voznesenskii, *Neft*, 1935, **6**, No. 2, 14; *Chem. Abs.*, 1936, **30**, 4306; *J. Inst. Pet. Tech.*, 1936, **22**, 356A.

[21] Y. I. Khisin and L. R. Sungalovskaya, *J. Applied Chem. (U.S.S.R.)*, 1936, **9**, 731; *Chem. Abs.*, 1936, **30**, 7831; *Brit. Chem. Abs.* **B**, 1936, 626.

[22] Referred to by V. Parkhomenko, *Neft*, 1932, **3**, No. 3-4, 30; *Chem. Abs.*, 1935, **29**, 2702. *Cf.* Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**, 1014.

[23] K. P. Likhushin, A. A. Dei-Karkhanova and N. B. Shaknovich, *Azer. Neft. Khoz.*, **1933**, No. 10-11, 116; *Chem. Abs.*, 1934, **28**, 7487.

[24] F. Shneider and A. Kheifetz, *Neft. Khoz.*, 1934, **26**, No. 5, 59; *Chem. Abs.*, 1934, **28**, 7488; *Brit. Chem. Abs.* **B**, 1935, 392.

[25] K. P. Likhushin, A. A. Dei-Karkhanova and M. I. Mirzakulieva, *Azer. Neft. Khoz.*, **1934**, No. 1, 63; *Chem. Abs.*, 1934, **28**, 7488.

Osborn and Craig[27] find that the fraction of petroleum hydrocarbons extracted by liquid sulphur dioxide is practically wholly composed of sulphonatable constituents. Such an extract is treated with an approximately equal proportion of 90 to 103 per cent sulphuric acid, and after the reaction, water is added to bring about stratification. The product is a concentrated solution of water-soluble sulphonic acids. This procedure is said to be advantageous in that it requires comparatively small bulks of corrosive acid and correspondingly smaller corrosion-resistant apparatus.

EXTRACTION AND PURIFICATION OF THE PETROLEUM SULPHONATES

In recovering the sulphonic acids derived from petroleum oils, two general methods are employed: the selective solvent action of the lower monobasic alcohols and precipitation of the petroleum sulphonate salts by salting out.[28] Thus, Ramayya[29] dissolves the organic acid constituents in acid sludge by treatment with 25 to 75 per cent aqueous ethyl alcohol. Reddish and Myers[30] employ an analogous process, and recommend that the proportion of sludge to alcohol be such that there is less than 20 per cent by weight of sulphonic acids in the final alcoholic solution. Buc[31] suggests that the extraction be made with a 50 per cent aqueous solution of isopropyl or higher water-soluble alcohol. The sulphonates taken up by the alcoholic solution are purified by precipitating the ionizable salts in an aqueous layer formed by a dehydrating agent such as sodium carbonate monohydrate. The dehydrating agent is added, separation takes place, and the two solutions are separately distilled to recover, from the alcoholic layer, the sulphonates, and from the aqueous layer, the sodium carbonate for further use as dehydrating agent. The method is said to be advantageous in that it permits purification with but a single distillation and extraction process.

Salting-out of sulphonates is advocated in some instances as a method of securing only the more desirable compounds. Thus, acid sludge is neutralized with sodium hydroxide and the aqueous solution treated with 2 to 15 per cent of sodium chloride to precipitate the sodium sulphonates.[32] Fussteig[33] reports, on the other hand, that the resulting products are often contaminated with portions of neutral oil. The latter may be removed, however, by extracting an aqueous alkaline solution of the sulphonates with acetone or ether. Vesterdal and Carlson[34] find that refining of green-acid salts may be effected by fractional precipitation from an aqueous solution of the salts by means of water-soluble organic liquids (such as acetone or alcohol) and salt. As the temperature of the solution is lowered, the sulphonate fractions separate out. If the acid sludge is neutralized with an aqueous lime slurry instead of sodium hydroxide, the insoluble alkaline-earth metal salts of the sulphonic acids are formed. Pilat and Sereda[35] mix the mass of precipitated sulphonates, asphaltenes, tars and resinous compounds from such a treatment with alkali carbonates, thereby converting the sulphonates into water-soluble compounds which are afterwards removed by extraction.

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[26] Dutch P. 36,949, 1935, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 2748.

[27] R. T. Osborn and R. Craig, U. S. P. 1,955,859, April 24, 1934, to Standard Oil Co. of Calif.; *Brit. Chem. Abs.* **B**, 1935, 182; *Chem. Abs.*, 1934, **28**, 4215.

[28] So greatly do acid sludges vary in nature that no generalization is entirely safe. It is best to say only that a certain sludge, treated in the described manner, will yield products suitable for applications suggested. E. Holzman and S. Suknarowski (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 378; *Chem. Abs.*, 1936, **30**, 275) have developed a system of analysis that can be applied to these sludges that may be of assistance in determining what treatment would be best adapted to a particular sludge.

[29] K. S. Ramayya, U. S. P. 1,956,592, May 1, 1934; *Brit. Chem. Abs.* **B**, 1935, 89; *Chem. Abs.*, 1934, **28**, 4215.

[30] W. T. Reddish and L. D. Myers, U. S. P. 1,960,828, May 29, 1934, to Twitchell Process Co.; *Brit. Chem. Abs.* **B**, 1935, 294; *Chem. Abs.*, 1934, **28**, 4590.

[31] H. E. Buc, U. S. P. 1,981,799, Nov. 20, 1934, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1935, 984; *Chem. Abs.*, 1935, **29**, 589.

[32] German P. 604,641, 1934, to Chem. Fabrik Pott and Co.; *J. Inst. Pet. Tech.*, 1935, **21**, 101A; *Chem. Abs.*, 1935, **29**, 919.

[33] R. Fussteig, *Chimie et industrie*, 1933, **30**, 1027; *Brit. Chem. Abs.* **B**, 1934, 83; *Chem. Abs.*, 1934, **28**, 2169.

[34] H. G. Vesterdal and E. W. Carlson, U. S. P. 2,035,106, March 24, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 3216.

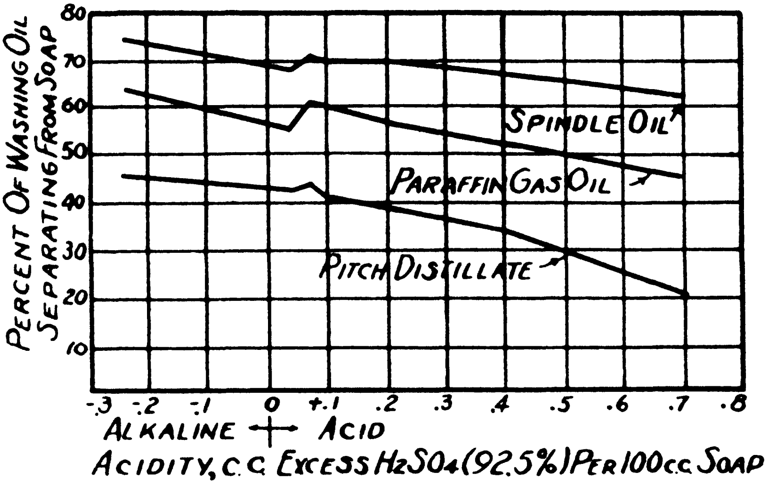

FIG. 258.—Effect of Soap Acidity on Separation of Light Hydrocarbon Oil from Green-Acid Soap. (R. E. Beard and E. N. Roberts)

Ramayya[36] refined crude oil-soluble mahogany sulphonates by dissolving them in an aqueous solution of a lower monohydric alcohol (such as isopropanol). The solution is separated from the sludge, and agitated with a light petroleum distillate. On settling, the solvent layer is separately collected and evaporated to recover the refined salts. Extraction with propane, at 50 to 95°C. and under sufficient pressure to maintain the hydrocarbon in the liquid state, has been suggested.[36a] Beard and Roberts[37] remove these mahogany acids from acid-treated oils by taking advantage of the differential solubility of their salts in a green-acid soap solution (an aqueous solution of neutralized green acids). This relationship is shown by the graphs in Figs. 258 and 259. Thus, an acid-treated oil is neutralized with caustic soda and extracted with about 12½ (volume) per cent of a 10 per cent aqueous solution of green-acid soap. Practically all the mahogany-acid salts are taken up in this soap, separated from the refined, finished oil. The green-acid solution is acidified with 0.5 to 1.0 cc. of 92.5 per cent sulphuric acid per 1000 cc. of soap solution. The specified amount of acid is chosen since, at this acidity, the mahogany acids are more soluble in oil than in green-acid soap solution, and can be extracted by a light petroleum distillate. Further, the degree of acidity assures a clean-breaking emulsion of the light distillate and the soap. The light distillate extract is removed and evaporated to recover the mahogany components, and by neutralizing the green-acid soap solution it may be reused as an extracting medium. A flow diagram of the procedure is shown in Fig. 260.

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[35] S. Pilat and J. Sereda, U. S. P. 1,933,070, Oct. 31, 1933; *Chem. Abs.*, 1934, **28**, 630.

[36] K. S. Ramayya, U. S. P. 1,930,488, Oct. 17, 1933; *Brit. Chem. Abs.* B, 1934, 789; *Chem. Abs.*, 1934, **28**, 307. See also L. D. Meyers and L. A. Stegemeyer, U. S. P. 2,068,149, Jan. 19, 1937, to Twitchell Process Co.

[36a] M. H. Arveson, U. S. P. 2,059,838, Nov. 3, 1936, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1937, **31**, 538.

[37] R. E. Beard and E. N. Roberts, U. S. P. 1,997,566, April 16, 1935, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 3822; *Brit. Chem. Abs.* B, 1936, 438.

Many other methods for refining petroleum sulphonates have been proposed. For example, Limburg[38] suggests treating an aqueous solution of the sulphonates with an organic base such as aniline, which forms insoluble compounds with the sulphonates. Instead of forming a salt with an ammonia derivative, Bird and Rosen[39] purify the water-soluble salts by a double extraction process, involving the usual crude separation of the sulphonates in an alcohol, and a subsequent refining in liquid ammonia. These investigators report that liquid ammonia acts as a highly selective solvent for the lower water-soluble sulphonic acids. The ammonia solution of the sodium sulphonates is filtered, and the filtrate evaporated, to obtain the purified sulphonates. The powder so obtained consists of the purified, relatively low molecular weight, fraction of the sodium sulphonates. It is lighter in color than the crude mixture of sulphonates used as starting material, and is re-

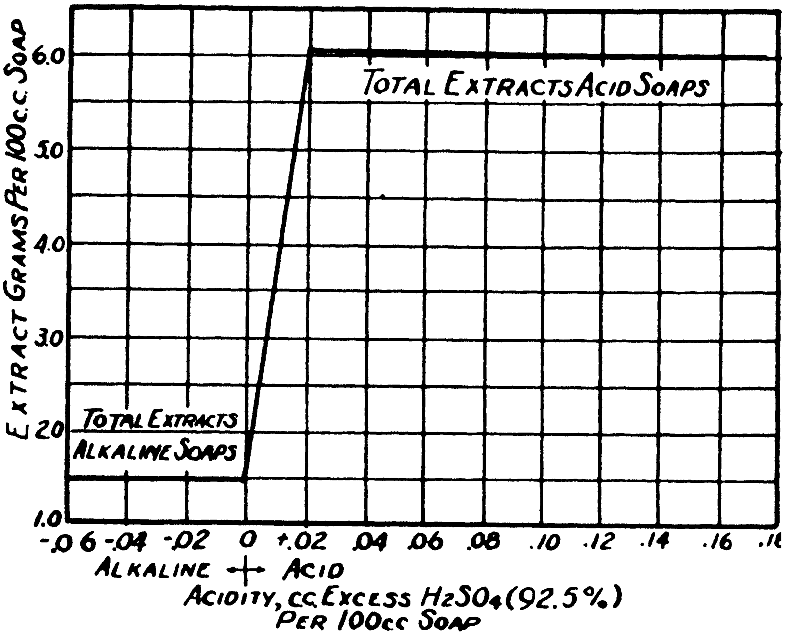

FIG. 259.—Influence of Soap Acidity on Efficiency of Light-Oil Extraction of Green-Acid Soaps. (R. E. Beard and E. N. Roberts)

ported to be more effective as a wetting agent. Another proposed method of separation involves osmosis of the dissolved sulphonates against water.[40]

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[38] H. Limburg, U. S. P. 1,937,521, Dec. 5, 1933, to Flintkote Corp.; *Brit. Chem. Abs.* **B**, 1934, 824; *Chem. Abs.*, 1934, **28**, 1056.

[39] J. Bird and R. Rosen, U. S. P. 1,963,257, June 19, 1934, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1935, 345; *Chem. Abs.*, 1934, **28**, 5272.

It is reported that naphthenic acids, obtained in alkali treatment of burning oils, may be employed in the extraction of petroleum sulphonic acids.[40a] Dennemark[41] points out that the latter compounds, particularly those derived from naphthenes, may be freed of sulphuric acid by dialysis.

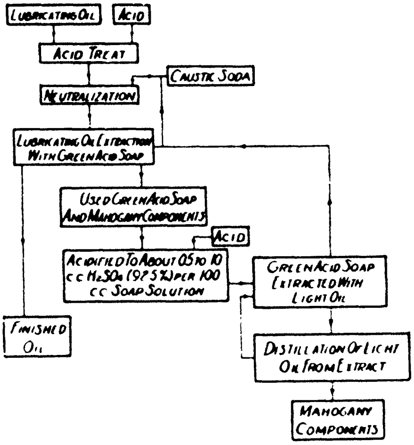
LUBRICATING OIL
ACID
ACID TREAT
CAUSTIC SODA
NEUTRALIZATION
LUBRICATING OIL EXTRACTION WITH GREEN ACID SOAP
USED GREEN ACID SOAP AND MAHOGANY COMPONENTS
ACID
ACIDIFIED TO ABOUT 0.5 TO 1.0 CC H2SO4 (92.5%) PER 100 CC SOAP SOLUTION
GREEN ACID SOAP EXTRACTED WITH LIGHT OIL
FINISHED OIL
DISTILLATION OF LIGHT OIL FROM EXTRACT
MAHOGANY COMPONENTS

FIG. 260. Flow Sheet for Separation of Mahogany Components from Green-Acid Soaps Employed in Lubricating Oil Refining. (R. E. Beard and E. N. Roberts)

INDUSTRIAL APPLICATIONS OF PETROLEUM SULPHONIC ACIDS AS DETERGENTS

The petroleum sulphonic acids are mildly detergent, and their stability to hard water, acid and alkaline solutions makes them useful in some applications. Liberthson[41a] has prepared water-soluble petroleum sulphonates in flakes by extracting the green acids, converting these to water-soluble salts, and taking up the salts in a solvent. The resulting solution is applied in a thin film to a smooth heated metal surface, and the subsequent evaporation causes a deposition of solid laminar fragments which can readily be dislodged and collected. Other investigators recommend preparing the sulphonates in a concentrated solution. Hintzmann[42] finds that the sodium sulphonates are more soluble in aqueous solutions of urea or thiourea than in pure water and suggests this as a means of making a concentrated solution. As an example, 35 parts of sodium sulphonate with 17 parts of urea were dissolved in 45 parts of warm water. Some of the alkali metal sulphonates tend to form turbid solutions in water, which Diependruck[43] reports can be clarified by the addition of approximately 15 per cent of a highly refined spindle or cylinder oil. The detergent and cleaning properties can be enhanced, it has been reported, by mixing the acid sludge sulphonates with an alkali metal alkyl hydrogen sulphate

[40] F. Berl, British P. 426,785, 1935; *Brit. Chem. Abs.* **B**, 1935, 539; *Chem. Abs.*, 1935, **29**, 6332.

[40a] P. G. Montag and P. I. Romashenko, Russian P. 23,914, 1931, to Gosudarstvennoe Ob'edinenie Azerbaidzhanskoi Neftyanoi Promuishlemnosti "Asneft"; *Chem. Abs.*, 1936, **30**, 8594.

[41] A. E. Dennemark, Russian P. 21,128, 1931; *Chem. Abs.*, 1936, **30**, 8599.

[41a] L. Liberthson, U. S. P. 1,947,861, Feb. 20, 1934, to L. Sonneborn Sons, Inc.; *Brit. Chem. Abs.* **B**, 1934, 1048; *Chem. Abs.*, 1934, **28**, 2890.

[42] K. Hintzmann, German P. 612,417, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 4954.

[43] O. Diependruck, Canadian P. 354,565, 1935, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 1904.

of more than 10 carbon atoms per molecule.[44] Incorporation of the sulphonates is reported to materially increase the solubility of the sulphate derivatives in water.[44a]

PETROLEUM SULPHONIC ACIDS IN EMULSIONS

Petroleum sulphonics may be employed in making stable hydrocarbon emulsions, and, conversely, may be used as constituents of emulsion-breaking mixtures. Gelbke[45] prepares an emulsifying agent useful in textile and leather work from the crude sulphonic acids. The acids are first dehydrated by treatment with superheated steam, followed by vacuum distillation. They are then dissolved in 94 to 98 per cent ethyl or methyl alcohol and the solution allowed to stand at 0°C. until clear. Distillation of the alcohol yields a product reputed to have high emulsifying power.

Limburg[46] recommends a specially treated spindle oil fraction as a source of petroleum sulphonic acids yielding calcium salts soluble in water and in aqueous solutions of calcium chloride. The spindle oil distillate is first treated with not less than 30 per cent of strong sulphuric acid, and after separation from this treatment the oil is subjected to the action of a second quantity of sulphuric acid. The acid sludge from the second treatment is neutralized, and the resulting salts furnish emulsifying agents capable of stabilizing aqueous emulsions of mineral and vegetable oils and asphalts. Liberthson[47] stabilizes an asphalt emulsion with mixed green-acid salts. The acids are freed of non-acid oily materials by solution in an alcohol of low molecular weight, such as ethanol, and after recovery from this solution are converted to the water-soluble sodium or potassium salts.

Ramayya[48] suggests the use of a mixture of green and mahogany acids. The crude acids are freed of uncombined sulphuric acid (by extraction with isopropyl alcohol) and reacted with alkali or ammonium bases to form salts. Thirty per cent of mahogany acid salts similarly prepared are admixed. The water content should be less than 30 per cent, and under these circumstances the products are readily soluble in hydrocarbons and tend to form stable emulsions.

The emulsifying properties of the sulphonic acids can be enhanced by the addition of various other substances, such as a mixture of mahogany acids, a hydroxyamine of a fatty acid (e.g., triethanolamine oleate) and a homogenizer such as a polyhydric alcohol.[49] Chamberlain[49a] recommends that petroleum sulphonic acids be employed in conjunction with sulphonated castor oil. Sereda[50] suggests that adding mineral hydrocarbon oil, a protective colloid, and a small proportion of a finely divided, water-insoluble, substance such as kaolin to the sulphonic acids or their salts improves their emulsive powers. By combining a soluble deflocculent agent with sulphonic acids as emulsive agents, DeGroote[51] has produced a mixture stated to lessen clogging of pipe lines and oil wells containing flowing oil. The solid matter is kept in suspension in a non-flocculent condition by these agents, preventing accumulations of solid matter that tend to restrict the flow of the liquid.

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[44] British P. 423,768, 1935, to Standard Oil Development Co.; *J. Inst. Pet. Tech.*, 1935, **21**, 176A; *Chem. Abs.*, 1935, **29**, 4484.

[44a] Carleton Ellis, U. S. P. 2,071,512, Feb. 23, 1937, to Standard Oil Development Co.

[45] M. Gelbke, German P. 595,604, 1934, to Sudfeldt and Co.; *Chem. Abs.*, 1934, **28**, 5271.

[46] H. Limburg, U. S. P. 1,958,630, May 15, 1934, to Patent and Licensing Corp.; *Brit. Chem. Abs.* **B**, 1935, 216; *Chem. Abs.*, 1934, **28**, 4590.

[47] L. Liberthson, U. S. P. 1,940,807, Dec. 26, 1933, to L. Sonneborn Sons, Inc.; *Brit. Chem. Abs.* **B**, 1934, 868; *Chem. Abs.*, 1934, **28**, 1526.

[48] K. S. Ramayya, U. S. P. 1,935,666, Nov. 21, 1933, to L. Sonneborn Sons, Inc.; *Brit. Chem. Abs.* **B**, 1934, 789; *Chem. Abs.*, 1934, **28**, 887.

[49] British P. 444,851, 1935, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1936, 584. British P. 446,314, 1936; *Brit. Chem. Abs.* **B**, 1936, 629; *J. Inst. Pet. Tech.*, 1936, **22**, 318A. See also, A. Chwala and E. Waldmann, Austrian P. 134,993, 1933; *Chem. Abs.*, 1934, **28**, 913.

[49a] D. S. Chamberlain, U. S. P. 2,067,888, Jan. 19, 1937, to National Oil Products Co.; *Chem. Abs.*, 1937, **31**, 1639.

[50] J. Sereda, Austrian P. 136,996, 1934; *Chem. Abs.*, 1934, **28**, 4550.

[51] M. DeGroote, U. S. P. 1,892,205, Dec. 27, 1932, to Tretolite Co.; *Chem. Abs.*, 1933, **27**, 2029; *Brit. Chem. Abs.* **B**, 1933, 853.

The petroleum sulphonic acids are effective also in breaking emulsions of the water-in-oil type. Bukh, Pivovarova and Mirzoeva[52] report dehydrating a heavy Baku crude with 1 per cent of "black Kontakt" (petroleum sulphonates derived from an acid-treated kerosene fraction). The emulsion was broken at a temperature of 90 to 95°C., or even lower. It is suggested that this action is the result of the formation of oil-soluble calcium sulphonates by an interaction between the sulphonic acids and calcium naphthenates, and that calcium sulphonates thus formed bring about the separation. Bukh and Mirzoeva[53] add that they prefer the black Kontakt because of its cheapness, its consistency and the ease with which it can be handled. The actual treatment takes only 20 to 30 minutes; the entire operation approximately 1 hour. Fischer and Reddish[54] have proposed that ethyl alcohol be added to the petroleum sulphonates used in breaking emulsions of the water-in-oil type. They find that the alcohol acts as a viscosity reducing agent and accelerates coalescence. DeGroote and Keiser[55] use equal quantities of green and mahogany acids and add to them a strongly oxidized castor oil and about 10 per cent of kerosene for this purpose. An earlier suggestion made by DeGroote and Wirtel[56] involved the use of sodium petroleum sulphonates with a modified fatty acid partially saponified with ammonium hydroxide, and a hydrophobe solvent such as kerosene.

TEXTILE USES OF SULPHONIC ACIDS

Petroleum sulphonic acids have been suggested as wetting agents in dyeing operations, particularly when dyeing from an acid bath.[57] Under such conditions the fatty acid soaps break to fatty acids and sodium salts of the stronger acid present, the fatty acid interfering with, rather than aiding leveling of the dyestuff. The sulphonic acid wetting agents are stable under acid conditions, and efficient leveling action is said to be obtained. To prepare such an agent, Lievre[58] recommends that the oils present first be removed from the neutralized solutions obtained from acid sludge by steam distillation. The product is acidified with sulphuric acid and redistilled to remove any volatile impurities that may be formed. The refined acids are then dried and may be employed as wetting agents. MacLaren[59] reported that the sulphonation products of a specially prepared cracked distillate boiling above 230°C. are best suited to the preparation of wetting agents. The heavy "pressure tar" residue from high-pressure, high-temperature cracking stills is distilled, and the fraction boiling above 230°C. collected. According to this investigator, the material should have a sulphuric absorption between 12 and 20 per cent, a hexane solubility of 99.8 to 100 per cent, and less than half of one per cent of carbon residue. This heavy mixture is sulphonated in a cooled mixer, maintaining the temperature below 100°C. The reaction takes place almost instantaneously, to produce yields of sulphonic acids as high as 55 to 70 per cent. Baddiley and Chapman[60] have also found that best results are obtained from wetting agents composed of the sulphonation products of oils boiling above 230°C. However, they obtain their sulphonatable material from a sulphur dioxide extract boiling above this temperature rather than from a cracked, refined distillate. Field[61] uses a slightly lighter sulphur dioxide extract derived from a kerosene distillate. The extract in this case boils in the range 180 to 280°C. and according to the investigator is almost entirely composed of aromatic and unsaturated hydrocarbons. These have a high sulphuric acid absorption, but it is recommended that in the sulphonation, sulphuric acid of strength not greater than 100 per cent be used, and further, that the amount of acid be insufficient to bring about complete sulphonation of all sulphonatable compounds, since it is believed that the more readily sulphonated compounds are more satisfactory both as wetting agents and as detergent compositions. May, Brodersen and Waldmüller[62] find that the low-boiling mineral oils can be sulphonated to produce wetting agents that are useful in a somewhat different field. Added to mercerizing lyes, these lighter sulphonates improve the wetting properties of the lyes with a reported improvement in the finish of the textiles treated.

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[52] D. N. Bukh, S. Pivovarova and E. Mirzoeva, *Azer. Neft. Khoz.*, **1933**, No 10, 48; *Chem. Abs.*, 1934, **28**, 7492.

[53] D. N. Bukh and E. Mirzoeva, *Azer. Neft. Khoz.*, **1933**, No. 5, 84; *Chem. Abs.*, 1934, **28**, 7493.

[54] C. Fischer and W. T. Reddish, U. S. P. 1,941,886, Jan. 2, 1934, to Kontol Co.; *Brit. Chem. Abs.* **B**, 1934, 918; *Chem. Abs.*, 1934, **28**, 1849.

[55] M. DeGroote and B. Keiser, U. S. P. 1,984,633, Dec. 18, 1934, to Tretolite Co.; *J. Inst. Pet. Tech.*, 1935, **21**, 98A; *Chem. Abs.*, 1935, **29**, 916.

[56] M. DeGroote and A. F. Wirtel, U. S. P. 1,940,398, Dec. 19, 1933, to Tretolite Co.; *Chem. Abs.* 1934, **28**, 1516.

[57] German P. 578,775, 1933, to A. Rechberg G.m.b.H., Georg Braun G.m.b.H. and Eduard Voit; *Chem. Abs.*, 1934, **28**, 913.

[58] G. P. Lievre, French P. 42,888, 1933, addition to French P. 751,422; *Chem. Abs.*, 1934, **28**, 1487.

[59] F. H. MacLaren, U. S. P. 1,999,128, April 23, 1935, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1935, **29**, 4162.

Various investigators have proposed that certain other compounds be added to the petroleum sulphonate wetting agents. For instance, such substances as benzene- or naphthalene-sulphonic acids have been suggested by Todd,[63] who reports that such compositions yield wetting agents readily soluble in cold water. Linder and Zickermann[64] propose that a mixture of a higher boiling mineral oil with an aliphatic alcohol or carboxylic acid (of not more than 10 carbon atoms) or with phenols be treated with 100 to 200 per cent of the calculated quantity of a strong sulphonating and dehydrating agent, such as chlorosulphonic acid. The products are said to be effective wetting agents.

Kennedy[65] has suggested a method of standardized classification to make possible an intelligible evaluation of various wetting agents. He proposes that the agent be rated on the basis of (a) the time required for pieces of cloth (1 cm. square) to sink in a solution containing the wetting agent, (b) the surface tension effect as measured by capillary rise, (c) the stability to hard water, (d) estimation of the fatty acid content and (e) a determination of Herbig's number.[66]

The mineral oil sulphonates have been suggested as media for carrying protective lubricants for use on yarns. Thus, Bouhuys[67] employs a mixture of mineral oil, mineral oil sulphonates, potassium soap, triethanolamine oleate and a soap-solvent, e.g., diethylene glycol, for this purpose. Such a composition does not have to be removed before the dyeing operation. On the other hand, Reddish[68] has proposed a composition that, while it is not left on the fibers during dyeing, is capable of a "self-scouring" action so that no outside agent need be employed to remove it. Refined mahogany sulphonates freed of entrained neutral oil components are used to make water-soluble a mineral white oil which acts as the lubricant. The proportions of sulphonates may vary from 7½ to 25 per cent of the oil-mahogany sulphonate mixture. According to this investigator, the resultant oil is a satisfactory lubricant for weaving, spinning or knitting operations, filming over the fibers or absorbed by the fibers very readily due to the low interfacial tension between the oil and the textile fiber. Furthermore, the oil can be removed at any time by immersion in water without the use of fatty acid detergents or alkalies. Since the oil is stable, any traces that may linger are not affected by the dyeing operation, nor do they inhibit dyeing or wetting out of the fabric or become rancid in stored cloth and thus give rise to offensive odors.

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[60] J. Baddiley and E. Chapman, German P. 594,260, 1934, to British Dyestuffs Corp.; *Chem. Abs.*, 1934, **28**, 3575.

[61] E. Field, U. S. P. 2,036,469, Apr. 7, 1936, to Standard Oil Co. of California; *Chem. Abs.*, 1936, **30**, 3627.

[62] R. May, K. Brodersen and A. Waldmüller, German P. 588,351, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 1551.

[63] W. Todd, British P. 406,001, 1934, to Imperial Chemical Industries, Ltd.; *Chem. Abs.*, 1934, **28**, 4930; *Brit. Chem. Abs.* **B**, 1934, 355.

[64] K. Linder and J. Zickermann, German P. 614,227, 1935, to Oranienburger Chem. Fabrik. A.-G.; *J. Inst. Pet. Tech.*, 1935, **21**, 424A; *Chem. Abs.*, 1935, **29**, 5952.

[65] T. Kennedy, *Dyer*, 1935, **74**, 389; *Chem. Abs.*, 1936, **30**, 2664. Also, K. Linder (*Chem. Ztg.*, 1935, **59**, 388; *Brit. Chem. Abs.* **B**, 1935, 617) has shown that sulphonic acid content can be distinguished from the sulphuric ester content by hydrolyzing the esters with boiling hydrochloric acid and extracting with diethyl ether.

[66] Herbig's number is determined by immersing the fabric in the test solution, centrifuging and weighing, all operations being conducted under specified conditions. The wetting power of water is taken as unity: W. Herbig and H. Seyferth, *Z. deut. Oel-Fett-Ind.*, 1925, **45**, 751; *Chem. Abs.*, 1926, **20**, 1142; *Melliand. Textilber.*, 1927, **8**, 45, 149; *Chem. Abs.*, 1927, **21**, 2068.

[67] A. G. Bouhuys, U. S. P. 1,979,188, Oct. 30, 1934, to American Enka Corp.; *Brit. Chem. Abs.* **B**, 1935, 943; *Chem. Abs.*, 1935, **29**, 356.

[68] W. T. Reddish, U. S. P. 1,909,721, May 16, 1933, to Twitchell Process Co.; *Brit. Chem. Abs.* **B**, 1934, 188; *Chem. Abs.*, 1933, **27**, 3834.

Reddish[69] has also suggested mahogany sulphonates as an aid to alkali used in boiling out the naturally present oil and waxes in cotton, jute and similar materials. Removal of these bodies is necessary since they render the fibers water-repellent and hence resistant to bleaching and dyeing. The addition of 0.1 to 2.0 per cent of refined mahogany sulphonates to the alkali bath serves as an activator. This is said to make the process more rapid and correspondingly milder, since the need of pressure-boiling or strong alkalies is obviated.

INSECTICIDES

As a wetting agent and vehicle in insecticides the petroleum sulphonates have several advantages. Petrov, Isachenko and Goritzkaya[70] have shown that the mixed petroleum sulphonates and mineral oils (Kontakt) are more toxic than nicotine sulphate and casein in hard water. The maximum mortality (of the insects) obtained using nicotine sulphate, soap, casein and water was 32 per cent, while with a nicotine solution one-fifth as strong plus 0.5 per cent of Kontakt, a 45 per cent mortality was recorded. A Kontakt solution (1.5 per cent) caused a 25 per cent mortality. Hessle[71] has proposed a spray consisting of non-toxic hydrocarbon oils, and an aqueous solution of toxic sulphones and sulphonates from acid sludge. A number of similar insecticides have been described by Savel'ev.[72] These are formulated as concentrates to be mixed with water and are based largely on green acids as emulsifying agents mixed with various petroleum fractions (such as kerosene, lubricating oil or the like).

Another proposal[72a] is to dissolve sulphur dioxide in a mineral (or castor) oil containing mahogany acids. The composition may be emulsified with water. Volck[73] prefers an aqueous solution of a fatty acid soap in which are dissolved sufficient free fatty acid to render the solution neutral, casein and salts of petroleum sulphonic acids.

Martin[73a] finds that petroleum calcium γ-sulphonates are effective spray

[69] W. T. Reddish, U. S. P. 1,991,335, Feb. 12, 1935, to Twitchell Process Co.; *Brit. Chem. Abs.* **B**, 1936, 96; *Chem. Abs.*, 1935, **29**, 2370.

[70] A. D. Petrov, V. B. Isachenko and O. V. Goritzkaya, *Bull. Plant Protection (U.S.S.R.)*, 1931, **3** (1), 189. *Foreign Pet. Tech.*, 1933, 1 (2), 39; *J. Inst. Pet. Tech.*, 1934, **20**, 382A; *Chem. Abs.*, 1933, **27**, 5876.

[71] E. T. Hessle, U. S. P. 1,921,158, Aug. 8, 1933, to Mid-West Chem. Co.; *Brit. Chem. Abs.* **B**, 1934, 518; *Chem. Abs.*, 1933, **27**, 5140. See also. W. H. Volck, U. S. P. 1,922,607, Aug. 15, 1933, to California Spray Chemical Corp.; *Brit. Chem. Abs.* **B**, 1934, 469; *Chem. Abs.*, 1933, **27**, 5141. French P. 798,734, 1936; *Chem. Abs.*, 1936, **30**, 7274.

[72] A. I. Savel'ev. *Foreign Petr. Techn.*, 1933, 1 (2), 40; *J. Inst. Pet. Tech.*, 1934, **20**, 382A.

[72a] K. T. Steik and J. F. Muller, U. S. P. 2,068,089, Jan. 19, 1937, to National Oil Products Co.; *Chem. Abs.*, 1937, **31**, 1547.

[73] W. H. Volck, U. S. P. 2,056,238, Oct. 6, 1936, to Calif. Spray-Chemical Corp.; *Chem. Abs.*, 1936, **30**, 8508.

[73a] H. Martin, *Fertilizer, Feeding Stuffs and Farm Supplies J.*, 1934, **19**, 674; *Chem. Abs.*, 1935, **29**, 1203.

spreading agents when used in a concentration of 2 pounds per 100 gallons of spray solution. The γ-sulphonates are satisfactory in conjunction with any toxic agent now employed in practice as spreader agents, and are also useful as emulsifying agents in preparing petroleum oil-lead arsenate sprays. The β-sulphonates have excellent spreading properties, but are ineffective in the presence of copper, lead or calcium salts due to the formation and precipitation of the heavy-metal compounds.

Peairs and Gould[74] report that nicotine sulphate and Penetrol (a commercial sulphonated oxidized petroleum oil preparation) was the most successful insecticide tested for controlling the pistol case-bearer.

Grant[75] has suggested that pyrethrum or derris be extracted in a solvent composed of kerosene or light lubricating oil (31 parts), oil soluble sulphonates (18.4 parts) and water (2 parts). This solvent solution can be modified by the addition of isopropyl or higher alcohols. The mixture is said to be advantageous in that it is not sensitive to the presence of water in the vegetable matter being extracted, and can, in consequence, be used in making insecticide concentrates from moist materials.

Marx and Brodersen[76] have prepared a fungicide employing mineral oil sulphonates and dispersed sulphur.

MISCELLANEOUS USES OF PETROLEUM SULPHONATES

Fedotov[77] pointed out some years ago that ammonium sulphate and a mixture of alkali and alkaline earth metal sulphonates would serve as a leather softener in the tanning industry, and that in the chrome tanning process the same mixture would serve as a reducing agent. Later Fridlyand[78] tested this suggested process and reported that it gave good results and could be used in place of the usual sulphite on calf skins. Bazarova[79] also investigated the possibilities of the petroleum oil sulphonates as reducing agents in chrome tanning to replace the glucose solution. His results showed that these substances (Kontakt) worked well, the reduction proceeding as follows:

$$
\begin{aligned}
&12K_2Cr_2O_7 + 11H_2SO_4 + C_{14}H_{16}SO_3 + 17H_2O \longrightarrow 12Cr_2(OH)_6 + 14CO_2 + 12K_2SO_4\\
&12K_2Cr_2O_7 + 23H_2SO_4 + C_{14}H_{16}SO_3 \longrightarrow 12K_2SO_4 + 12Cr_2(OH)_4SO_4 + 14CO_2 + 7H_2O\\
&12K_2Cr_2O_7 + 35H_2SO_4 + C_{14}H_{16}SO_3 \longrightarrow 12K_2SO_4 + 24Cr(OH)SO_4 + 14CO_2 + 31H_2O\\
&12K_2Cr_2O_7 + 47H_2SO_4 + C_{11}H_{16}SO_3 \longrightarrow 12K_2SO_4 + 12Cr_2(SO_4)_3 + 14CO_2 + 55H_2O
\end{aligned}
$$

It is reported[80] that petroleum sulphonates obtained in manufacturing white oils will serve as solvent activators to speed the mastication of rubber, if added to such a vehicle as mineral seal oil. King and King reported that petroleum sulphonates mixed with mineral seal oil serves as a thermoplasticizing compound for use with rubber.[81] Gorsuch and Kinney[82] propose an emulsion of glycerol, alcohol, mineral oil, rosin soap and mahogany sulphonates to prevent rubber sticking during vulcanization.

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[74] L. M. Peairs and E. Gould, *J. Econ. Entom.*, 1930, **23**, 188; *Chem. Abs.*, 1930, **24**, 3315.

[75] D. H. Grant, U. S. P. 1,940,646, Dec. 19, 1933, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1934, 853; *Chem. Abs.*, 1934, **28**, 1460.

[76] K. Marx and K. Brodersen, German P. 579,701, 1933, to I. G. Farbenind A. G.; *Chem. Abs.*, 1934, **28**, 1134. See also V. A. Sebastian, French P. 737,963, 1931; *Chem. Abs.*, 1933, **27**, 1709.

[77] A. A. Fedotov, Russian P. 4,556, 1924; *Chem. Abs.*, 1928, **22**, 4869.

[78] A. A. Fridlyand, *Ovladenie Tekhnikoi: Kozhobuvnoe Proizvodstvo*, **1932**, No. 5, 40; *Chem. Abs.*, 1933, **27**, 6010.

[79] D. Bazarova, *Kozhevenno-Obrivnaya Promuish. U.S.S.R.*, 1934, **13**, 121; *J. Inst. Pet. Tech.*, 1935, **21**, 143A; *Chem. Abs.*, 1934, **28**, 6017.

[80] British P. 398,702, 1933, to Robert J. King Co., Inc.; *Chem. Abs.*, 1934, **28**, 1891; *Brit. Chem. Abs.* **B**, 1933, 979.

[81] R. J. King and E. C. King, U. S. P. 2,000,028, May 7, 1935, to Robert J. King Co., Inc.; *Chem. Abs.*, 1935, **29**, 4211.

[82] E. H. Gorsuch and A. M. Kinney, U. S. P. 1,927,066, Sept. 19, 1933, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1933, **27**, 6023; *Brit. Chem. Abs.* **B**, 1934, 639.

A number of lubricating compositions have been prepared with petroleum sulphonates, such as an extreme pressure lubricant made from a high-quality lubricating stock by incorporation of a lead salt of the oil-soluble mahogany sulphonates.[83] Adding a sodium salt of a mahogany sulphonate together with 5 to 30 per cent of a calcium soap, 15 to 20 per cent of petrolatum to a hydrocarbon oil and sufficient water for emulsification produces a stable, non-sweating grease.[84] Gay[85] reports a stable cutting-oil emulsion made up of 1 part of mahogany sulphonates, 0.5 part of alkali metal rosin soaps together with mineral oil and not more than 14.5 per cent of water. Brunstrum and Hilliker[86] compound a plug valve lubricant (for steam lines) from graphite, anhydrous calcium soap and a lead mahogany sulphonate soap.

The emulsive powers of the sulphonates make them useful in polishing compounds. Lewers[87] prepares a water-in-oil polishing wax from 30 parts of carnauba wax, 20 parts of paraffin wax, 120 parts of naphtha, 4 parts of heavy mineral oil and 10 parts of oil-soluble petroleum sulphonates in 300 parts of water. Mahogany sulphonates have been employed[88] in making a liquid coating compound from casein, glue or other water-insoluble colloid and oil with pigments or fillers.

Water-soluble petroleum sulphonates have been suggested as dust fixatives. The sulphonates (as sodium salts) in 15 per cent aqueous solution are mixed with a hygroscopic agent such as glycerol and a plasticizing agent such as glucose. This mixture is sprayed on the dust, and it is reported that the surface becomes covered with a solid layer of cemented dust.[89]

Oil-soluble dyes can be prepared from water-soluble dyestuffs with the aid of mahogany sulphonates. This has been accomplished in two ways: by forming a true compound between a basic-reacting, water-soluble dye; and by causing the oil-soluble sulphonate to absorb a quantity of a concentrated aqueous solution of the dyestuff. In the former process the dye (Victoria Green, Bismarck Brown or Methylene Blue, for example) is reacted in an acidified aqueous solution with the sulphonic acid (usually present as an alkali metal salt).[90] In the latter method, no true compound is formed, but the mahogany sulphonate acts to form an optically clear dispersion of a water-soluble dye throughout oils, fats and waxes. According to Straus[91] oil-soluble dyes and shades are restricted in number and variety. They are, furthermore, less resistant to the action of light than are available water-soluble colors. Sulphonic dispersion makes more varied water soluble dyes available as oil-soluble dyes. The dispersion is prepared, for example, by grinding together two parts of Patent Blue A, Color Index 714, 10 parts of purified, oil-soluble mineral oil sulphonate, 12 parts of mineral white oil and 10 parts of water. The action in the present case depends on the fact that mahogany sulphonates are capable of absorbing a certain quantity of water without losing the property of dissolving in oil, and that this absorbed water may be present as a concentrated solution of a water-soluble dyestuff.

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[83] French P. 779,896, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 5648.

[84] British P. 436,998, 1935, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1936, 9; *Chem. Abs.*, 1936, **30**, 2366.

[85] N. N. Gay, U. S. P. 2,036,470, April 7, 1936, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 3638. *Cf.* H. E. Buc, U. S. P. 2,052,164, Aug 25, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 6853.

[86] L. C. Brunstrum and W. P. Hilliker, U. S. P. 1,982,200, Nov. 27, 1934, to Standard Oil Co. of Ind.; *Brit. Chem. Abs.* **B**, 1936, 309; *Chem. Abs.*, 1935, **29**, 598.

[87] W. W. Lewers, U. S. P. 1,986,936, Jan. 8, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 1150; *Chem. Abs.*, 1935, **29**, 1541.

[88] H. Heckel, U. S. P. 2,001,422, May 14, 1935, to Emery Industries, Inc.; *Brit. Chem. Abs.* **B**, 1936, 510; *Chem. Abs.*, 1935, **29**, 4481.

[89] F. M. Archibald, U. S. P. 1,995,598, March 26, 1935, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1936, 597; *Chem. Abs.*, 1935, **29**, 3132.

[90] H. E. Buc, U. S. P. 1,841,876, Jan. 19, 1932, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1933, 262; *Chem. Abs.*, 1932, **26**, 1798.

[91] J. Straus, U. S. P. 1,996,391, April 2, 1935; *Brit. Chem. Abs.* **B**, 1936, 445; *Chem. Abs.*, 1935, **29**, 3526.

In combination with fatty acids, such as stearic, mahogany sulphonates have been found useful in preventing foaming in emulsions. Buc[92] suggests a combination of one part of stearic acid, 99 parts of oil-soluble sulphonates and 500 parts of heavy mineral white oil. This combination may be added to 5,000 parts of water to form a stable, non-foaming emulsion. By incorporating 3 per cent of mahogany sulphonates with 97 per cent of mineral white oils, Mathias[93] makes a foam-preventing mixture for use in beet-sugar refining. Bird[94] reports that the water-soluble sulphonic acids may be added to aqueous solutions, such as sugar solutions, to precipitate coloring matter and substances rendering the solution cloudy. The water soluble acids are added, to bring about precipitation of their insoluble alkaline earth salts. The salts come out of solution in such a form as to be highly adsorbent, carrying with them coloring matter present in the solution.

McIntyre and Higgins[95] report that a specially prepared mahogany sulphonate can be treated to meet the government requirements for a fat-denaturant. Acid oils obtained in refining are treated with 5 to 30 pounds of 98 per cent sulphuric acid for each 50 gallons of oil, and the sludge settled out. The latter is washed with about an equal amount of water, and this is then drawn off leaving the sulphonates. Neutralized with sodium hydroxide, washed with water and reduced, they are mixed with the fats to be denatured with or without the application of heat.

Medicinal products have been prepared from sulphur-bearing mineral or shale oils, particularly those containing more than 2 per cent of sulphur. Wernicke[96] recommends that these oils be refined under such conditions as will not reduce the sulphur content, e.g., with alkali solution, sulphuric acid of 40 to 75 per cent concentration, aluminum chloride or bleaching earth. Sulphonation is then effected at a low temperature, yielding transparent products of alleged therapeutic value.[97] Hessle[98] makes a sulphonated product reputed to be of therapeutic value by reacting a hydrocarbon oil with sulphur in the presence of an iron oxide catalyst. This product is treated with oleum (30 per cent free sulphur trioxide), and the resulting sulphonated compounds precipitated. After washing with brine they are extracted with benzene, neutralized with alkali hydroxide and the solvent evaporated. The resultant product is a reducing agent, and if specially dehydrated in a vacuum dryer produces a fluffy yellow powder inflammable in air.

According to Nazarov and Khain[99] petroleum sulphonic acids are effective as catalysts in preparing esters, being as effective as sulphuric acid in this synthesis. Isopropyl acetate was made by reacting the alcohol and acetic acid at 105 to 110°C. at a feed rate of 1 cc. per minute and an alcohol-acid ratio of 4.22 to 1.

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[92] H. E. Buc, U. S. P. 2,052,164, Aug. 25, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 6853.

[93] H. Mathias, U. S. P. 1,964,641, June 26, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1934, **28**, 5153; *Brit. Chem. Abs.* B, 1935, 387.

[94] J. C. Bird, U. S. P. 2,025,715, Dec. 31, 1935, to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1936, 816; *Chem. Abs.*, 1936, **30**, 914.

[95] G. McIntyre and E. J. Higgins, Canadian P. 338,557, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1934, **28**, 2209.

[96] E. A. Wernicke, British P. 432,797, 1934; *Brit. Chem. Abs.* B, 1935, 937; *Chem. Abs.*, 1936, **30**, 606.

[97] These sulphur-bearing oils are known by the general term "ichthyols," particularly those containing very considerable percentages of organic sulphur. J. A. Riddick (*Field and Lab.*, 1936, **4**, 33; *Chem. Abs.*, 1936, **30**, 5365) reports that such an oil may be obtained by the destructive distillation of a bituminous rock found near Burnet, Texas. The oil so obtained is dark red, and contains about 10 per cent of organic sulphur. The oil is sulphonated and the resulting acids neutralized with ammonium hydroxide to produce the ichthyol of commerce. The product so obtained contains about 48 per cent of water, 5.5 to 6.3 per cent ammonium sulphate, and the remainder is the ammonium ichthyolsulphonate. Riddick gives some discussion of the therapeutic value of these oils. For further discussion of the preparation of these materials, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[98] E. T. Hessle, U. S. P. 1,996,334, April 2, 1935, to Thiophene Products Co.; *Chem. Abs.*, 1935, **29**, 3468.

[99] S. A. Nazarov and S. S. Khain, *Materials on Cracking and Chemical Treatment of Products Obtained, Khimteoret (Leningrad)*, **1935**, No. 2, 183; *Chem. Abs.*, 1935, **29**, 6032. See also J. N. Zaganiaris and G. A. Varvoglis, *Ber.*, 1936, **69**, 2277; *Chem. Abs.*, 1937, **31**, 368.

The yield amounted to 97 per cent on the anhydrous acetic acid or 94 per cent on the original material. With technical grade materials, the yield falls to 73 per cent on the anhydrous acid (42 per cent on the technical 58 per cent acetic acid). Only 8.2 g. of the petroleum sulphonates were used per kilogram of the acetate. Similar experiments with secondary butyl and amyl alcohols gave equally good results.

Virobyantz[100] reports that treatment of a petroleum fraction (containing aromatics) with 97 to 99 per cent sulphuric acid for five hours, followed by settling and separation of the sulphonic acids, makes possible a 90 per cent recovery of aromatics. The sulphonic acids are readily decomposed by dilution with water and distillation with superheated steam. Hydrolysis begins at 140°C. and is practically complete at 210°C. The recovered aromatics afterwards are freed of acidic bodies and dried.

Petrov[101] reports that high molecular weight sulphonic acids can be condensed with aldehydes, in the presence of aromatic amines, to form resins applicable in varnishes and lacquers. Langedijk[102] has prepared the heavy metal salts of petroleum oil sulphonates and finds them available as siccatives for use in paints and varnishes. A brushless shaving cream, described by Ferguson,[102a] is composed of water, stearic acid, a fatty oil and the water-soluble salt of a sulphonated (or sulphated) aliphatic hydrocarbon. The latter should contain 10 to 18 carbon atoms per molecule.

Another use suggested for sulphonic acids is as a coagulating agent for carbon in the recovery of sulphuric acid from acid sludge.[103]

SULPHONATION OF OLEFINS

Though the discussion in this chapter has been primarily the sulphonation of paraffin and aromatic hydrocarbons of petroleum, the sulphonation and sulphation of olefins simultaneously present is necessarily of interest and industrially of increasing importance. Some of the reactions of the olefins with sulphuric acid (sulphation) have been discussed in other chapters,[103a] and attention now will be directed only to sulphonation reactions.

When ethylene is absorbed in sulphuric acid of more than 100 per cent concentration, carbyl sulphate is formed.[104] This substance is becoming of greater importance as uses are developed for it and its hydrolysis product, isethionic acid. Carbyl sulphate itself can be converted to acetic acid according to Merley and Spring[105] by a process involving neutralization and hydrolysis. The sulphate is hydrolyzed by the addition of water, and the solution neutralized with caustic soda. Some of the sodium sulphate formed is separated out by cooling and the liquor is then heated with calcium hydroxide and excess sodium hydroxide. Sodium acetate thus formed is acidified with the hydrolyzed carbyl sulphate liquors from the first step of the process and fractionally distilled to yield free acetic acid. The hydrolysis product of carbyl sulphate, isethionic acid, is the source of the sulphonate group in an important class of sulphonate detergents, the Igepons.

[100] R. A. Virobyantz, *Neft. Khoz.*, 1933, **25**, 160; *J. Inst. Pet. Tech.*, 1934, **20**, 415A; *Chem. Abs.*, 1934, **28**, 3227.

[101] G. S. Petrov, Russian P. 37,845, 1934; *Chem. Abs.*, 1936, **30**, 1901.

[102] S. L. Langedijk, U. S. P. 1,947,652, Feb. 20, 1934, to Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.* **B**, 1934, 1094; *Chem. Abs.*, 1934, **28**, 2926.

[102a] R. H. Ferguson, Canadian P. 356,798, 1936, to Procter and Gamble Co. of Canada, Ltd.; *Chem. Abs.*, 1936, **30**, 3172.

[103] A. B. Brown and D. V. Bransky, U. S. P. 2,022,800, Dec. 3, 1935, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1936, **30**, 851; *Brit. Chem. Abs.* **B**, 1936, 1031.

[103a] See Chapters 13, 14 and 15 for production of alcohols from olefins; Chapter 26 for polymerization of olefins by means of sulphuric acid.

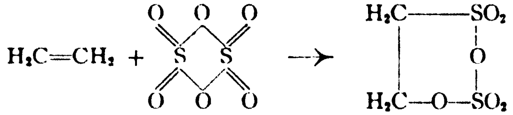
[104] See Chapter 13; also, B. T. Brooks, *Ind. Eng. Chem.*, 1935, **27**, 278; *Chem. Abs.*, 1935, **29**, 2700; *Brit. Chem. Abs.* **B**, 1935, 536.

[105] S. R. Merley and O. Spring, U. S. P. 1,904,160, April 18, 1933, to Doherty Research Co.; *Brit. Chem. Abs.* **B**, 1933, 998; *Chem. Abs.*, 1933, **27**, 3224.

Michael and Weiner[106] have investigated the action of oleum on ethylene in some detail and concluded from their results that the reaction proceeds either (1) by the addition of pyrosulphuric acid (present in equilibrium with sulphuric acid) according to the mechanism:

$$H_2C{=}CH_2 + HOSO_2OSO_2OH \longrightarrow HO_3SCH_2CH_2OSO_3H$$

to produce ethionic acid; or (2) when the anhydride is present in excess (since sulphur trioxide cannot add directly) the dimer, S_2O_6, present in equilibrium in the solution, adds to form carbyl sulphate as follows:[107]



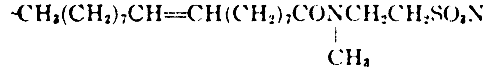
Adams, Eatough and Marvel[108] report that the reaction product of an olefin and sulphur trioxide can be transformed by concentrated hydrogen chloride into a chloroalkane sulphonic acid, such as chloroethanesulphonic acid.

THE SULPHO DETERGENTS

Two principal types of these detergents are being marketed: the true sulphonates and the sulphuric acid esters of high molecular weight alcohols (produced by hydrogenation of the corresponding fatty acids).[109] Representative of the former class are the Igepons A and T. Igepon A is the condensation product of isethionic acid and oleic acid corresponding to the formula,

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_2CH_2SO_3Na$$

and is reported to be a good detergent, fairly stable to acid solutions though subject to hydrolytic splitting at the carboxyl group in alkaline solutions. Igepon T was developed to overcome this fault and stands up better in both alkaline and acid solutions.[109a] The formula of Igepon T is,



$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO\underset{\displaystyle CH_3}{\underset{|}{N}}CH_2CH_2SO_3Na$$

Numerous methods of producing the sulphonated substances have been proposed. One method comprises treating aliphatic or cycloaliphatic compounds with sulphuric acid or other sulphonating agent in the presence of an organic solvent inert to the acid. Thus, if carbon tetrachloride is used, the reaction products are allowed to settle and the excess sulphuric acid is found in the lower layer, the solvent carrying the sulphonation products in the upper layer.[110]

Fulton and Vesterdal[111] prepared sulphate detergents which were said to be suitable for use with sea water. A mixture of olefins (containing octenes and higher members) obtained from oil cracking is treated with fuming sulphuric acid below 5°C. After reaction, the mixture is made alkaline and heated in order to decompose any unstable compounds present. The desired soap is then separated from this mixture. A flow sheet of their procedure is given in Fig. 261.

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[106] A. Michael and N. Weiner, *J.A.C.S.*, 1936, 58, 294; *Chem. Abs.*, 1936, 30, 2922.

[107] It should be noted that these investigators do not agree with the mechanism proposed by H. Wieland and E. Sakellarios (*Ber.*, 1920, 53, 203; *Chem. Abs.*, 1920, 14, 2636) who suggest that strong inorganic acids add as basic addenda —OH and acidic radicals. Thus, sulphuric acid would add as —OH and —SO_3H.

[108] R. Adams, H. Eatough and C. S. Marvel, U. S. P. 2,036,249, April 17, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, 30, 3442. See also, British P. 444,639, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, 30, 5596; *Brit. Chem. Abs.* B, 1936, 683.

[109] To simplify discussion of these high molecular weight alcohols, the name "hymolal" has been suggested (*Ind. Eng. Chem., News Edition*, 1934, 12, 98). The wetting and cleansing agents derived from them are "hymolal salts," of which class sodium lauryl sulphate is an example. See also. Swiss P. 156,087, 1932, to H. Th. Böhme A.-G.; British P. 354,851, 1932; *Chem. Abs.*, 1932, 26, 5773; and British P. 357,649, 1932, to H. Th. Böhme A.-G.; *Chem. Abs.*, 1932, 26, 6083; *Brit. Chem. Abs.* B, 1932, 56.

[109a] R. A. Duncan, *Ind. Eng. Chem.*, 1934, 26, 24; *Chem. Abs.*, 1934, 28, 1144; *Brit. Chem. Abs* B, 1934, 285.

[110] French P. 773,656, 1934, to Henkel & Cie. G.m.b.H.; *Chem. Abs.*, 1935, 29, 1436.

[111] S. C. Fulton and H. G. Vesterdal, U. S. P. 2,049,055, July 28, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, 30, 6592.

On the other hand a sulphonic acid can be made, in addition to methods previously mentioned, by oxidation of the corresponding thiosulphate. If sodium dodecanethiosulphate is oxidized with sodium permanganate, aqueous nitric acid or hydrogen peroxide, the corresponding sodium dodecanesulphonate can be obtained.[112] An analogous method suggested by Keller[113] uses a sulphurated technical mixture of paraffin hydrocarbons of 8 or more carbon atoms (made by treating a mixture of chlorinated paraffinic compounds with an alcoholic solution of potassium sulphide). This mixture is treated with an oxidizing agent such as nitric acid, hydrogen peroxide or a dichromate to produce the corresponding sulphonic acids. Partially oxidized stages of this reaction yield acids said to have good emulsive power.

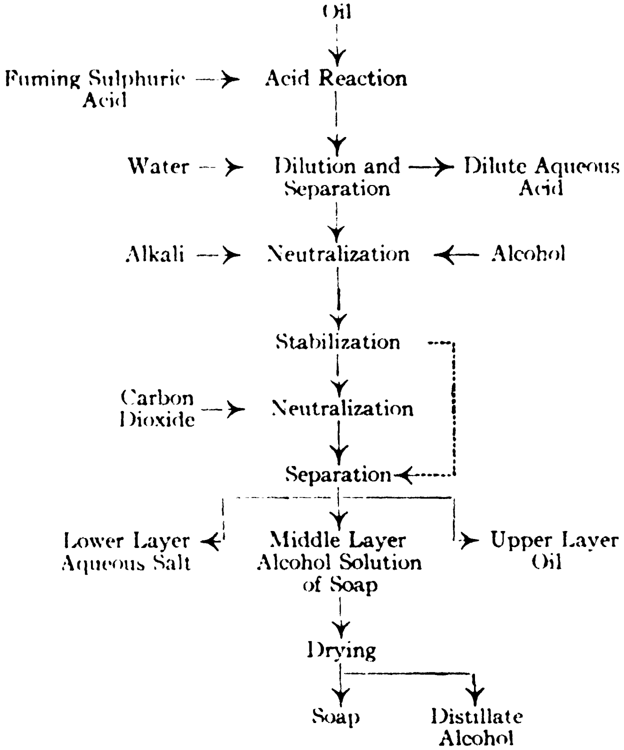

FIG. 261.—Flow Sheet for Manufacture of Sulphate Detergents from Cracked Oils. (S. C. Fulton and H. G. Vesterdal)

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[112] British P. 439,177, 1934, to Henkel & Cie. G.m.b.H.; *Brit. Chem. Abs.* B, 1936, 138.

[113] K. Keller, U. S. P. 1,925,191, Sept. 5, 1933, to General Aniline Works; *Chem. Abs.*, 1933, 27, 5337.

Investigations of the detergent properties of Igepon A and T carried out by Boedeker[114] showed that 3 per cent solutions of these substances contained no colloidal particles and behaved as true solutions, while similar warm solutions of sodium stearate and oleate contained particles visible in the ultramicroscope. Cooling the stearate solution below 20°C. caused it to gel due to the formation of closely interlocked needle crystals. A 20 per cent solution of sodium oleate showed similar properties. The addition of 16 per cent (by weight on the sodium stearate or oleate) of Igepon A to such a solution prevents the formation and precipitation of insoluble calcium and magnesium soaps in hard water.

Lederer[115] found that Igepon A and T show emulsification, foaming and surface tension lowering properties similar to those of soaps although in equally concentrated solutions the interfacial tension with oil is much lower when the Igepons are used than under the action of soaps. This investigator reports the percentage composition of the Igepons as follows:

	Igepon A %	Igepon T %
Active substance	45	33.5
Soap	4	2.5
Salts	16	8.0
Water	35	56.0
Molecular weight	412	425

Though general application of the sulpho detergents may be limited by their higher cost, many special uses have been developed where their desirable qualities more than offset this factor. Special formations as flakes or filaments[116] aid in rapid solution. Their ability to resist acid is taken advantage of in removing pitch (originating from the branding of sheep) from raw wool. The latter is treated in a fulling mill with one of these detergents, and when the pitch has been removed the solution is withdrawn and fulling carried out as usual.[117] By using a water-soluble alcohol, dilute acetic acid and one of the acid-stable sulpho detergents, colored carpets can be cleaned and their brightness restored without removing naturally present protective oils and fats.[118]

Representative of the second class of sulpho detergents, i.e., those containing the sulphate group, is sodium oleyl sulphate:

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2OSO_3Na$$

or sodium lauryl sulphate:

$$CH_3(CH_2)_{10}CH_2OSO_3Na$$

The sulphated products are made from saturated alcohols (having 10 to 14 carbon atoms) which in turn are obtained by hydrogenating cocoanut or palm kernel oils. The sodium salt of the sulphated product is marketed in the textile trade as "Gardinol WA." The oleyl sulphate is made by sulphating the alcohol (generally produced by hydrogenating material obtained from sperm oil), but in this process it is difficult to avoid some sulphation of the double bond, so that the technical sodium salt is generally a mixture of the sulphate ester and the sulphonate.[119] Siebenbürger[120] finds, however, that the sulphation can be directed to a certain

[114] K. Boedeker, *Melliand Textilber.*, 1932, 13, 436; *Chem. Abs.*, 1933, 27, 3341.

[115] E. L. Lederer, *Angew. Chem.*, 1934, 47, 119; *Chem. Abs.*, 1934, 28, 2931; *Brit. Chem. Abs.* B, 1934, 332.

[116] A. Welter, French P. 758,733, 1934; *Chem. Abs.*, 1934, 28, 3261.

[117] German P. 625,173, 1936, to Oranienburger chem. Fabrik. A.-G.; *Chem. Abs.*, 1936, 30, 3256.

[118] British P. 419,846, 1934, to N. V. Koninklijke Vereen Tapijtfabrieken; *Brit. Chem. Abs.* B, 1935, 98; *Chem. Abs.*, 1935, 29, 3176.

[119] R. A. Duncan, *Ind. Eng. Chem.*, 1934, 26, 24; *Chem. Abs.*, 1934, 28, 1144; *Brit. Chem. Abs.* B, 1934, 285.

[120] H. Siebenbürger, U. S. P. 2,060,254, Nov. 10, 1936, to Society of Chemical Industry, Basle.

extent. If the sulphonation be carried out by treating the higher alcohol to be sulphonated with the addition product of a liquid organic base (such as pyridine or dimethylaniline) and sulphur trioxide, practically all sulphonation will take place at the hydroxyl group of the alcohol, according to this investigator. From analytical figures, it was found that the product obtained by this type of procedure consists only of the sulphuric acid ester salt, while the double-bonded alcohols might be sulphated similarly without addition at the unsaturated linkage. The properties of these sulphate detergents parallel fairly closely those of the sulphonate detergents

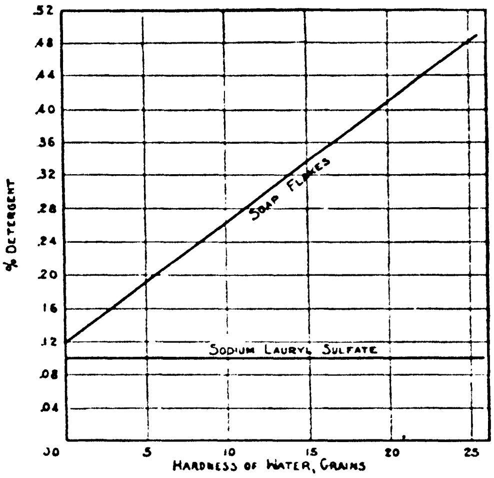

Fig. 262.
Comparison of Quantities of Soap Flakes and of Sodium Lauryl Sulphate Required for Washing in Water of Varying Hardness. (R. A. Duncan)

Courtesy Industrial and Engineering Chemistry

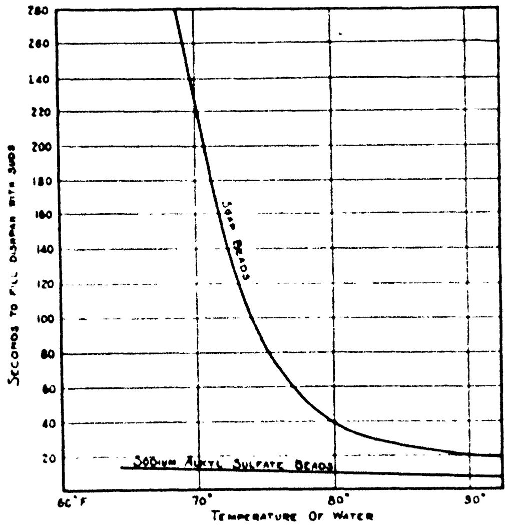

Fig. 263.
Time Required for Equal Amounts of Suds to Form with 0.42 Ounce (12 g.) of Soap Beads and with 0.21 Ounce (6 g.) of Sodium Alkyl Sulphate in 1 Gallon of Water (15-Grain Hardness). (R. A. Duncan)

Courtesy Industrial and Engineering Chemistry

and are used in much the same ways as wetting and detergent agents in textile uses and as emulsifying and demulsifying agents. Thus, Neville and Jeanson[121] reported that the sulpho detergents react similarly in their absorption rates in alkaline and acidic solutions and in their effects on dye absorption. Using wool as a standard fabric and working with both Gardinol CA (a sulphate) and Igepon T (a sulphonate), it was found that these substances may, under varying conditions, aid or retard dye absorption, while the absorption of the wetting agent itself varies widely with the *p*H value of the solution, being so rapidly absorbed in strongly acid solutions as to be uneconomic.

Aside from the sulphation of the high molecular weight alcohols, other methods have been proposed for producing the sulphated type of aliphatic substance. Thus Kalischer and Biehler[122] make the sulphated aliphatic acids and esters by treating the corresponding aliphatic hydroxy or unsaturated acid with the product obtained by reacting acetic anhydride with oleum. Bertsch[123] suggests treating similar aliphatic acids, such as ricinoleic, with a low-weight alcohol such as isobutyl, and a sulphating agent, or, alternatively, using isobutylsulphuric acid as sulphating agent.

The detergent action of the sulphates has been used in de-inking waste paper. It is proposed that a substance such as sodium lauryl sulphate be used with a halogenated hydrocarbon solvent or with fuller's earth. The treatment may be carried out in a hollander, the solution separated for reuse, and the washed pulp remade into paper.[124] Leathermann[125] uses the wetting properties of the sulphate salts in fireproofing a fabric. The cloth is saturated with a 1 per cent solution of sodium lauryl sulphate, wrung out and impregnated with sodium stannate. After drying it is immersed in an aqueous ferric chloride solution. Washed and re-dried, it is then impregnated with chlorinated rubber and can be dyed if desired. Ellis[126] reports that the solubility of sulphate detergents in water, as well as their cleansing action, is increased by incorporation of water-soluble mineral-oil sludge sulphonates. He proposes that the sulphate derivatives be prepared from alcohols obtained on the oxidation of paraffin wax. The detergent compositions may be admixed also with hydroformed or hydrofined naphthas.

The sulphates are frequently used as constituents in agents designed to break water-in-oil emulsions. An ammonium salt of oleic hydrogen sulphate has been proposed for this purpose[127] and also such substances as the sulphuric acid ester of a high molecular weight alcohol (of from 12 to 26 carbon atoms)[128] or the sodium salt of a sulphate derived from tetradecyl alcohol.[129]

[121] H. A. Neville and C. A. Jeanson, III, *Am. Dyestuff Reptr.*, 1933, **22**, 541, 618; *J. Phys Chem.*, 1933, **27**, 1001; *Chem. Abs.*, 1933, **27**, 5986; *J. Inst. Pet. Tech*, 1934, **20**, 25A.

[122] G. Kalischer and F. Biehler, German P. 606,776, 1934, to I. G. Farbenind A.-G.; *Chem. Abs.*, 1935, **29**, 2976.

[123] H. Bertsch, U. S. P. 2,032,313, Feb. 25, 1936, to H. Th. Böhme A.-G.; *Chem. Abs.*, 1936, **30**, 2577. See also, German P. 549,667, 1930, to I. G. Farbenind. A.-G.

[124] British P. 438,403, 1935, to Deutsche Hydrierwerke A.-G.; *Chem. Abs.*, 1936, **30**, 3237.

[125] M. Leatherman, U. S. P. 1,961,108, May 29, 1934, to United States of America; *Brit. Chem Abs.* **B**, 1935, 304; *Chem. Abs.*, 1934, **28**, 4597.

[126] Carleton Ellis, U. S. P. 2,071,512, Feb. 23, 1937, to Standard Oil Development Co.

[127] M. DeGroote, B. Keiser and A. F. Wirtel, U. S. P. 1,926,715, Sept. 12, 1933, to Tretolite Co.; *Brit. Chem. Abs.* **B**, 1934, 748; *Chem. Abs.*, 1933, **27**, 5960.

[128] M. DeGroote and L. T. Monson, U. S. P. 1,938,323, Dec. 5, 1933, to Tretolite Co.; *Brit. Chem. Abs.* **B**, 1934, 870; *Chem. Abs.*, 1934, **28**, 1178.

[129] M. DeGroote, U. S. P. 1,943,815, Jan. 16, 1934, to Tretolite Co.; *Brit. Chem. Abs.* **B**, 1934, 870; *Chem. Abs.*, 1934, **28**, 2173.

Chapter 47

Chemical Action of Nitric Acid and Various Other Reagents on Saturated Hydrocarbons

The saturated paraffin and cycloparaffin hydrocarbons have often been regarded as very stable and inert substances which remain unaffected by most chemical reagents since all the carbon atoms in such hydrocarbons have their valences satisfied by hydrogen and other carbon atoms and therefore they would not be expected to undergo the numerous addition reactions characteristic of olefins and acetylenes. The results of many investigators have indicated, however, that the progressively higher members in a homologous series of the saturated hydrocarbons, and especially some of the branched-chain members, become more reactive toward many of the reagents which act upon aromatic hydrocarbons. Furthermore, the paraffins as a rule are especially susceptible to pyrolytic decomposition which not only results in the production of unsaturated and saturated compounds of lower molecular weight, but also the intermediate formation of free radicals which are usually much more reactive than the corresponding hydrocarbons.

Even after it was generally conceded that the higher paraffins were not inert bodies, this was still more or less the belief with respect to the lower (gaseous) members of the series, because, even though many of the liquid and solid paraffins were directly nitrated as early as 1880, this reaction had not been effected with the lower members (methane, ethane, propane and butane) as late as 1932. However, these lower members were successfully nitrated, in the vapor phase, about 1933. Apparently the gaseous cycloparaffins have not as yet been nitrated. Another reaction which appears to be of increasing importance to the paraffin hydrocarbons is the Friedel-Crafts reaction, which for many years was believed to be restricted entirely to aromatic compounds. All these and other factors should serve to create additional interest in the chemistry of the paraffin hydrocarbons in the future.

NITRATION OF PARAFFIN AND CYCLOPARAFFIN HYDROCARBONS

Although considerable work has been done on the direct nitration of the liquid and solid paraffin hydrocarbons since Meyer and Stüber[1] first prepared nitroparaffins in 1872 (from alkyl iodides and silver nitrite) it was not until about 1933 that direct nitration of the gaseous paraffins was successfully accomplished. Hass, Hodge and Vanderbilt[2] investigated the reaction of methane, ethane, propane and the two butanes with nitric acid in the vapor phase. Of these, they were able to nitrate all except methane. Small amounts of nitromethane were formed, however, during the nitration of the immediate homologues of methane.

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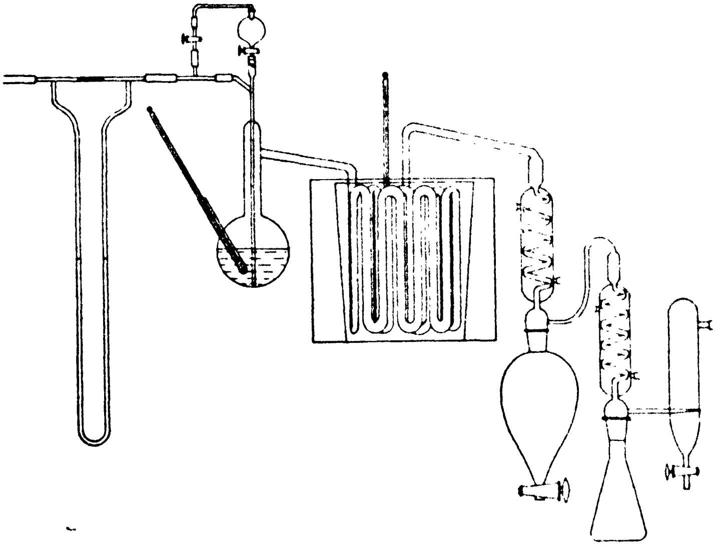
[1] V. Meyer and O. Stüber, *Ber.*, 1872, **5**, 203; *J.C.S.*, 1872, **25**, 474; *Chem. Zentr.*, 1872, 258. Also V. Meyer and co-workers, *Ber.*, 1872, **5**, 399, 514, 1029, 1034; *J.C.S.*, 1872, **25**, 682, 804; 1873, **26**, 261; *Chem. Zentr.*, 1872, 420, 580; 1873, 145, 146.

[2] H. B. Hass, E. B. Hodge and B. M. Vanderbilt, U. S. P. 1,967,667, July 24, 1934, to Purdue Research Foundation; *Chem. Abs.*, 1934, **28**, 5830; *Brit. Chem. Abs.* B, 1935, 618; *Ind. Eng. Chem.*, 1936, **28**, 339; *J. Inst. Pet. Tech.*, 1936, **22**, 203A; *Chem. Abs.*, 1936, **30**, 2918; *Brit. Chem. Abs.* A, 1936, 587. H. B. Hass and E. B. Hodge, U. S. P. 2,071,122, Feb. 16, 1937, to Purdue Research Foundation.

In the apparatus as shown in Fig. 264, hydrocarbon gases pass, at the rate of 150 liters per hour, through the flowmeter and then bubble through hot, concentrated nitric acid, the latter being added to the flask, as needed, from the dropping funnel as indicated. The mixed vapors of nitric acid and hydrocarbon then pass into the glass reactor (consisting of a series of U-bends) immersed in a eutectic mixture (molten) of sodium nitrite and potassium nitrate. The products issuing therefrom are recovered in condensers and a fog trap.

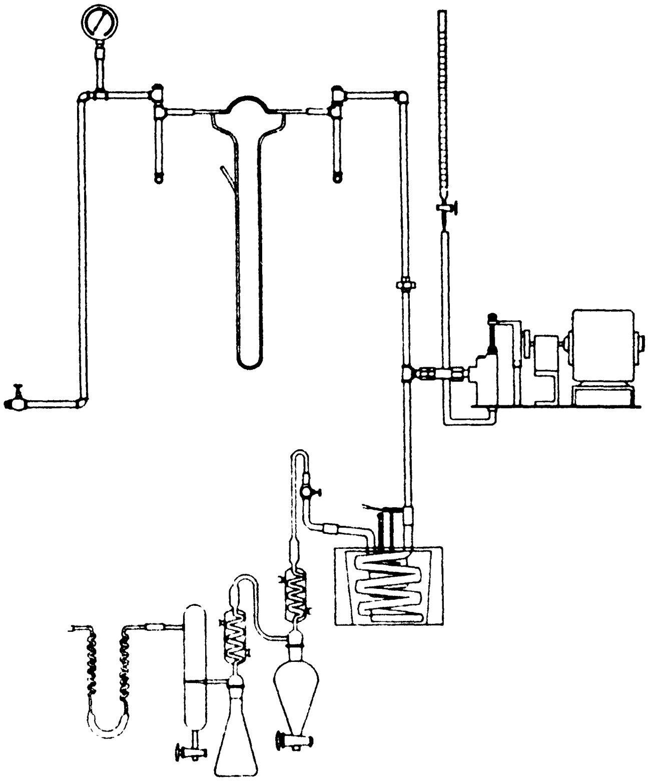
Hass and co-workers carried out their nitrations, both in batch and continuous processes, using concentrated nitric acid and the hydrocarbons under various pressures and at temperatures above the critical temperatures of the reactants so as to overcome certain difficulties such as immiscibility of the materials used. In the continuous process the hydrocarbon vapors were bubbled through hot concentrated nitric acid and the mixed vapors conducted into a reaction tube which was immersed in a molten salt bath heated to the desired temperature. After reaction the products were led into a condenser unit and finally into a fog trap and later separated by fractional distillation (Fig. 265). Oxidation always accompanied nitration and this was believed to result in the conversion of the paraffins to fatty acids which were then nitrated with the subsequent loss of carbon dioxide to give lower nitroparaffins. They also found that the isomeric products formed by nitration varied considerably with the temperature and permitted a certain measure of selectivity. For example, at 150°C. in sealed tubes, 2-methyl-2-nitropropane was the only nitro compound resulting from the nitration of isobutane, but, under atmospheric pressure and at 420°C., this isomer comprised only 7 per cent of the nitro compounds formed. No catalyst was found which aided nitration. Silica gel and platinum promoted oxidation rather than nitration.



Courtesy Industrial and Engineering Chemistry

FIG. 264.—Apparatus for Nitration of Gaseous Paraffin Hydrocarbons at Atmospheric Pressure. (H. B. Hass, E. B. Hodge and B. M. Vanderbilt)

The apparatus as shown in Fig. 265 operates in a manner similar to that of Fig. 264 except that superatmospheric pressures are employed. The main portion of the apparatus, including the reaction coil, however, is constructed of stainless steel instead of glass. The reactants (hydrocarbon and concentrated nitric acid) are introduced under pressure, the latter material being supplied by a stainless-steel pump. The products are recovered by condensation.



Courtesy Industrial and Engineering Chemistry

FIG. 265.—Apparatus for Vapor-Phase Nitration of Paraffin Hydrocarbons at Superatmospheric Pressure. (H. B. Hass, E. B. Hodge and B. M. Vanderbilt)

In Table 204 are shown the results of some of their experiments using a 2:1 molar mixture of hydrocarbon and nitric acid. The yields in the last column are based on the nitric acid used.

TABLE 204.—*Nitration of Gaseous Paraffins, 420°C., 1 Atm.*

Hydrocarbon	Acetone	Nitromethane	Nitroethane	1-Nitropropane	2-Nitropropane	1-Nitrobutane	2-Nitrobutane	1-Nitroisobutane	2-Nitroisobutane	Yields
						Per Cent				
Methane . .	—	—	—	—	—	—	—	—	—	0
Ethane	—	10 20	80-90	—	—	—	—	—	—	9
Propane . . .	—	9	(26?)	32	33	—	—	—	—	21
Butane	—	6	12	5	—	27	50	—	—	28
Isobutane . .	5	3	—	—	20	—	—	65	7	25

In Figs. 266, 267, and 268, are shown the rectification curves obtained with the products resulting from the nitration of isobutane, butane, and propane, respectively, at 420°C. and atmospheric pressure. Since the distillations were carried out under reduced pressure, the boiling points appearing on the curves have been corrected to 760 mm.

Although the direct nitration of methane appears not to have been attained, higher nitro compounds of methane have been prepared by nitration of compounds in which the methyl group occurs, for instance acetic anhydride. Krauz and Stepanek[3] described a process which is said to give yields of tetranitromethane as high as 95 per cent.

Fuming nitric acid, 65 parts, was distilled with 25 parts of phosphorus pentoxide, and the resulting nitrogen pentoxide added fo 100 parts of acetic anhydride. The mixing was accomplished very slowly, with constant stirring, while the temperature was maintained at 0°C. by ice cooling. The mix was then permitted to stand in ice water for 24 hours, and subsequently at laboratory temperature for 8 days. At the end of this period, it was poured into a large excess of cold water. The oil resulting was immediately separated, and washed with a 0.5 per cent aqueous solution of sodium bicarbonate, then with pure water, and dried with anhydrous sodium sulphate. By freezing out at 13°C., a yield of 95 per cent was obtained, the investigators reported. An attempt was made to prepare tetranitromethane by nitration of dimethylketone, but Krauz and Stepanek report obtaining a silver salt during the process which was unusually explosive. It was thought to be a salt of acetylmethylnitrolic acid.

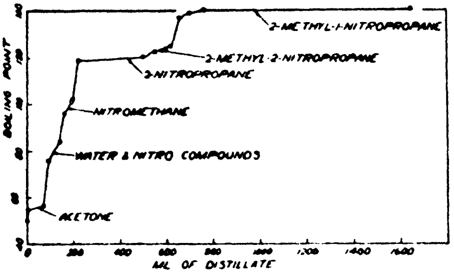


FIG. 266.
Rectification Curve for Products of Isobutane Nitration at 420°C. (H. B. Hass, E. B. Hodge and B. M. Vanderbilt)

Courtesy Industrial and Engineering Chemistry

Wyler[4] reports an analogous process of nitrating acetic anhydride to tetranitromethane, but this investigator finds that nitric acid may be used in place of nitrogen pentoxide, if catalysts such as phosphoric acid, phosphorus pentachloride, sulphuric acid, or sulphuryl chloride are present.

Nitration of many of the liquid paraffin hydrocarbons (for example, the pentanes, hexanes and heptanes) can be effected with nitric or fuming nitric acid.[5] Aliev and Gutuirya[6] found that saturated hydrocarbons do not react with hydrated aluminum nitrate [$Al(NO_3)_3$ $9H_2O$] at 95-100°C. Konowalow,[7] however, nitrated 2,7-dimethyloctane (possibly at a higher temperature) by heating it with this aluminum salt in an open vessel. Shoruigin and Topchiev[8] treated hexane, at 10-80°C., with nitrogen tetroxide (N_2O_4) diluted with carbon dioxide and obtained small yields (5-10 per cent) of 2-nitrohexane. Ultraviolet light was found to have no effect on the reaction. When toluene was nitrated under these conditions phenylnitromethane

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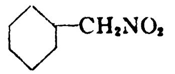
[3] C. Krauz and J. Stepanek, *Chem. Obzor*, 1935, **10**, 137; *Chem. Abs.*, 1936, **30**, 3403.
[4] J. Wyler, U. S. P. 2,057,076, Oct. 13, 1936, to Trojan Powder Co.; *Chem. Abs.*, 1936, **30**, 8247.
[5] Methods for nitrating such hydrocarbons are discussed by Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.
[6] P. M. Aliev and V. S. Gutuirya, *Ukrain. Khem. Zhur.*, 1934, **9**, 10; *Chem. Abs.*, 1935, **29**, 1770.
[7] M. I. Konowalow, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 109, 124; *J.C.S.*, 1907, **92** (1), 1; *Chem. Zentr.*, 1906, **2**, 312.
[8] P. P. Shoruigin and A. Topchiev, *Ber.*, 1934, **67**, 1362; *Chem. Abs.*, 1934, **28**, 6706.



and the ring-substituted mononitrotoluenes were obtained. The total yield of nitro compounds was increased by the use of ultraviolet light, although the relative proportions of the two types of products remained practically unchanged. They found also that cyclohexane reacted, at 30°C. and 80°C., with nitrogen tetroxide (N_2O_4) diluted with carbon dioxide, to give 20-25 per cent yields of nitrocyclohexane, and that the reaction was unaffected by ultraviolet light. Platonov and Shaikind[9] treated *n*-pentane, *n*-hexane, and *n*-heptane with nitric oxide (NO) at 450-500°C., using as catalyst kaolin mixed with the oxides of aluminum, cerium, and thorium. The products consisted of ammonia, nitric oxide, nitrogen, carbon monoxide, methane and unsaturated hydrocarbons. At 250-300°C., in the presence of vanadium pentoxide or platinum black, as catalysts, water, carbon monoxide, nitrogen, and unchanged hydrocarbons were formed. No carboxylic acids were detected among any of the products.[10]

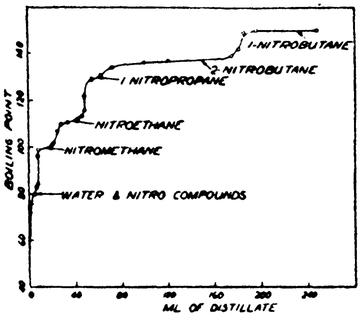


FIG. 267.
Rectification Curve of Products Formed in Nitration of Butane at 420°C. (H. B. Hass, E. B. Hodge and B. M. Vanderbilt)

Courtesy Industrial and Engineering Chemistry

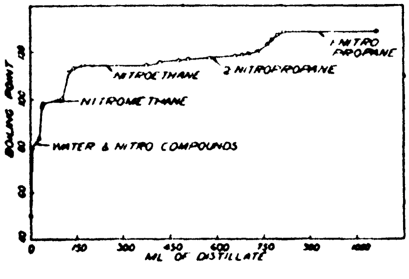


FIG. 268.
Rectification Curve for Products of Propane Nitration at 420°C. (H. B. Hass, E. B. Hodge and B. M. Vanderbilt)

Courtesy Industrial and Engineering Chemistry

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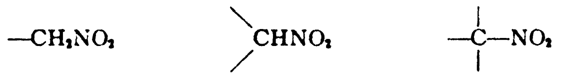
[9] M. S. Platonov and S. P. Shaikind, *J. Gen. Chem.* (*U.S.S.R.*), 1934, **4**, 434; *Brit. Chem. Abs.* **A**, 1934, 1329.

[10] R. H. McKee and R. H. Wilhelm (*Ind. Eng. Chem.*, 1936, **28**, 662; *Chem. Abs.*, 1936, **30**, 8180) report that nitrogen dioxide may be employed in nitrating benzene in the vapor phase, and state that in this reaction silica gel serves effectively as a catalyst. Yields as high as 83 per cent (based on benzene consumed) are said to result, and the production of by-products was not found

Nametkin and Nifontova[11] nitrated highly refined fractions of Grozny and American paraffin waxes with dilute nitric acid (sp. gr. 1.075) in sealed glass tubes at 125-130°C. From this they obtained a tertiary nitro compound ($C_{24}H_{49}NO_2$) melting at 29°C., a secondary nitro compound ($C_{24}H_{49}NO_2$) melting at 45° to 48°C., and an oil consisting of a dinitro compound [$C_{24}H_{48}(NO_2)_2$]. From this they concluded that these samples of paraffin wax contained about 25-30 per cent of isoparaffins. These same investigators[12] report that dilute nitric acid acts on another paraffin wax to yield a secondary nitro compound, $C_{26}H_{53}NO_2$, a smaller amount of the tertiary compound $C_{22}H_{45}NO_2$, and some of the dinitro compound $C_{22}H_{44}(NO_2)_2$. This wax consisted largely of *n*-alkanes, with not more than 10 per cent *iso*-alkanes.

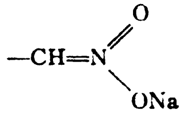
PROPERTIES OF NITRO COMPOUNDS OF PARAFFIN AND CYCLOPARAFFIN HYDROCARBONS

Of the three types of mononitro compounds, namely, primary, secondary, and tertiary, possessing the groupings shown below,

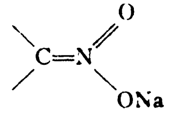


primary *secondary* *tertiary*

the first two are differentiated from the third by solubility in aqueous or alcoholic alkali solutions, in which the tertiary compounds are insoluble. This is due to the fact that the primary and secondary nitro compounds tautomerize in the presence of alkalies to the corresponding isonitroparaffins.[13] The structures of the sodium salts of these are shown below, in which form they are stable.

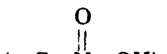


primary isonitro form



secondary isonitro form

If solutions of the salts of the isonitro compounds are acidified the first-formed yellow isonitro compounds



$(=C=\overset{\overset{\displaystyle O}{\|}}{N}-OH)$

rapidly change[14] to the colorless and stable normal form ($=CH-NO_2$). A study of the Raman effect of the nitromethanes[15] has substantiated the normal form as the one in which these compounds ordinarily exist.

The mononitro compounds of the lower paraffins are generally colorless liquids, possessing boiling points considerably higher than the corresponding hydrocarbons, usually distil without decomposition, and are sparingly soluble in water. The dinitro and trinitro compounds, also usually colorless, are high-boiling liquids or crystalline solids and many can be distilled with steam. Hunter and Marriott[16]

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to be excessive. Silica gel appears to have functioned as a dehydrating catalyst, as it does in numerous other reactions (e.g., esterification of acetic acid and alcohol). The product consisted largely of mononitrobenzene, though some nitrophenol was obtained, particularly in runs conducted at temperatures above 330°C. A temperature of 310°C. and an excess of nitrogen dioxide were required for the best yields. Some nitrogen dioxide was reduced to the monoxide, hydrogen being released as water. The monoxide may be reoxidized to nitrogen dioxide, however, by air oxidation.

[11] S. S. Nametkin and S. S. Nifontova, *J. Applied Chem.* (*U.S.S.R.*), 1933, **6**, 248; *Brit. Chem. Abs.* **B**, 1933, 692.

[12] S. S. Nametkin and S. S. Nifontova, *J. Applied Chem.* (*U.S.S.R.*), 1936, **9**, 462; *Chem. Abs.*, 1936, **30**, 7818; *Brit. Chem. Abs.* **B**, 1936, 627.

[13] J. U. Nef, *Ann.*, 1894, **280**, 263; *J.C.S.*, 1895, **68** (1), 3; *Chem. Zentr.*, 1894, **2**, 729.

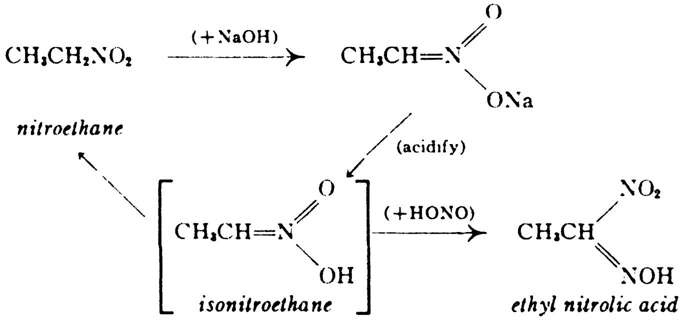
[14] A. F. Holleman, *Ber.*, 1900, **33**, 2913; *Chem. Zentr.*, 1900, **2**, 1104; *J.C.S.*, 1901, **80** (1), 3.

[15] L. Medard, *J. chim. phys.*, 1935, **32**, 136; *Chem. Abs.*, 1936, **30**, 1302.

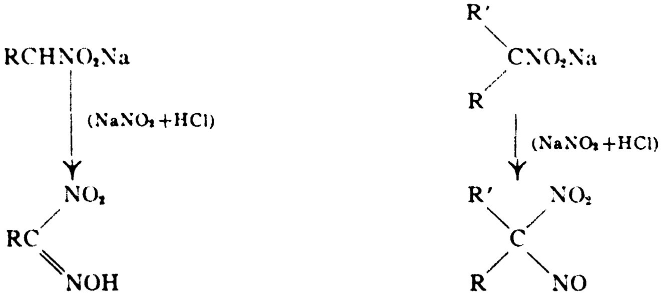
[16] L. Hunter and J. A. Marriott, *J.C.S.*, 1936, 285; *Brit. Chem. Abs.* **A**, 1936, 460; *Chem. Abs.*, 1936, **30**, 2929.

found, however, that nitrocyclohexane was somewhat unstable. Decomposition was most rapid and complete in open vessels, but occurs also in sealed tubes, yielding adipic acid in 1 to 4 weeks. Nitromethane, and some of the polynitro compounds, are not easily explosive, but Hass and co-workers[17] report that nitroethane, nitropropane, and the higher homologs are non-explosive. The corresponding mononitrates (e.g., methyl nitrate), on the other hand, are explosive according to Deniges.[18] Some of these nitric acid esters decompose explosively when warmed to yield, among other things, aldehydes and oxides of nitrogen. The rate of decomposition is, however, greatly decreased by an atmosphere of carbon dioxide. Thus, in a current of carbon dioxide, methyl nitrate, the most explosive of the series, could be distilled without explosion. The nitrates of secondary compounds, such as isopropyl nitrate, yielded the corresponding ketone and nitrogen oxides, this decomposition too being retarded by the presence of carbon dioxide.

The primary and secondary nitroparaffins are further differentiated by their ability to form nitrolic acids and pseudonitroles, respectively, when treated with alkaline solutions of sodium nitrite and subsequently acidified.[19] It has been shown that aqueous solutions of nitroethane are indifferent toward nitrous acid.[20] When freshly prepared solutions (from sodium nitroethane and hydrochloric acid), which contain isonitroethane, are used, however, a reaction occurs to give ethylnitrolic acid.



Primary nitroparaffins, with nitrous acid, give nitrolic acids which are red in solution. On the other hand, the secondary nitroparaffins yield pseudonitroles, which are blue in solution, while the tertiary nitro compounds do not react. These reactions are represented as follows:



nitrolic acid *pseudonitrole*

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[17] H. B. Hass, E. B. Hodge, and B. M. Vanderbilt, *Ind. Eng. Chem.*, 1936, **28**, 339; *Chem. Abs.*, 1936, **30**, 2918; *J. Inst. Pet. Tech.*, 1936, **22**, 203A; *Brit. Chem. Abs.* **A**, 1936, 587.

[18] G. Deniges, *Compt. rend.*, 1936, **202**, 1998; *Chem. Abs.*, 1936, **30**, 6703; *Brit. Chem. Abs.* **A**, 1936, 1094.

[19] J. Tscherniak, *Ann.*, 1876, **180**, 166; *J.C.S.*, 1876, **29**, 503. V. Meyer, *Ann.*, 1875, **175**, 88; *J.C.S.*, 1875, **28**, 557.

[20] A. Hantzch and H. Kissel, *Ber.*, 1899, **32**, 3137; *J.C.S.*, 1900, **78** (1), 89; *Chem. Zentr.*, 1900, **1**, 115.

The nitrolic acids are colorless or yellow bodies with acidic properties. They decompose slowly at room temperature and rapidly with the aid of heat to give the corresponding carboxylic acids, nitrogen tetroxide and nitrogen. With concentrated sulphuric acid they give carboxylic acids and nitrous oxide.[21] These reactions are illustrated by the following examples:

$$2RCH(NO)NO_2 \xrightarrow[\text{(heat)}]{} 2RCOOH + NO_2 + 1\tfrac{1}{2}N_2$$

$$RCH(NO)NO_2 \xrightarrow[(H_2SO_4)]{} RCOOH + N_2O$$

On reduction with tin and hydrochloric acid,[22] or sodium amalgam and water in the cold, they yield carboxylic acids, nitrous acid, and ammonia, with the intermediate formation of hydroxylamine. Wieland[23] obtained acethydroxylamine-oxime, $HO{-}NH{-}C(CH_3){=}NOH$, by the reduction of ethylnitrolic acid with sodium amalgam. Propyl pseudonitrole yields dimethylketoxime[24] when reduced with aluminum amalgam or ammonium sulphide. On oxidation with chromic acid the pseudonitroles are converted into dinitro compounds.[25] Further, the nitrolic acids and pseudonitroles are capable of diazotizing aniline.[26] The silver salts of nitrolic acids react with alkyl iodides to form colorless esters[27] and the sodium salts esterify with acid chlorides.[28]

The products formed by reduction of the nitro compounds depend largely on the conditions of reduction. For instance, nitromethane, treated with hydrogen[29] at 150-180°C. in the presence of nickel, gives methylamine, whereas, if stannous chloride[30] is employed as the reducing agent a mixture of methylamine and methylhydroxylamine is obtained. Nitroethane,[31] and also the primary mononitro compounds of hexane, heptane, and octane[32] furnish the corresponding primary amines on reduction with iron and acetic acid. Konowalow[33] treated 2-nitrohexane with zinc and acetic acid and obtained a mixture of 2-hexylamine and hexanone-2. From 2-nitro-2,3-dimethylbutane and 2-nitro-2,5-dimethylpentane, with tin and hydrochloric acid, he prepared the corresponding amines. On the other hand, 1-nitro-2,7-dimethyloctane gave a mixture of the corresponding primary amine and the aldehyde

$$(CH_3)_2CHCH_2CH_2CH_2CH_2CH(CH_3)CHO$$

when reduced under similar conditions. 2-Nitro-2,7-dimethyloctane, with tin and hydrochloric acid, furnished the corresponding amine. The secondary nitro compound (3- or 4-nitro-2,7-dimethyloctane) yielded a mixture of the secondary amine and the ketone when reduced in this manner.

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[21] V. Meyer, *Ann.*, 1875, **175**, 88; *J.C.S.*, 1875, **28**, 557. E. Demole, *Ann.*, 1875, **175**, 142; *J.C.S.*, 1875, **28**, 561. J. Tscherniak, *Ber.*, 1875, **8**, 114; *Chem. Zentr.*, **1875**, 162; *J.C.S.*, 1875, **28**, 560.

[22] V. Meyer and J. Locher, *Ann.*, 1876, **180**, 170; *J.C.S.*, 1876, **29**, 904.

[23] H. Wieland, *Ann.*, 1907, **353**, 65; *J.C.S.*, 1907, **92** (1), 494.

[24] A. Schöfer, *Ber.*, 1901, **34**, 1910; *J.C.S.*, 1901, **80** (1), 495. R. Scholl and K. Landsteiner, *Ber.*, 1896, **29**, 87; *J.C.S.*, 1896, **70** (1) 198; *Chem. Zentr.*, 1896, 1, 488.

[25] V. Meyer and J. Locher, *Ann.*, 1876, **180**, 133; *J.C.S.*, 1876, **29**, 904. G. Born, *Ber.*, 1896, **29**, 90; *J.C.S.*, 1896, **70** (1), 198; *Chem. Zentr.*, 1896, 1, 485. S. S. Nametkin, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 585; *J.C.S.*, 1910, **98** (1), 829.

[26] A. Schöfer, *loc. cit.* H. Wieland, *Ber.*, 1909, **42**, 816; *J.C.S.*, 1909, **96** (1), 217.

[27] O. Graul and A. Hantzsch, *Ber.*, 1898, **31**, 2854; *J.C.S.*, 1899, **76** (1), 187; *Chem. Zentr.*, 1899, 1, 28.

[28] V. Meyer, *Ber.*, 1894, **27**, 1600; *J.C.S.*, 1894, **66** (1), 436; *Chem. Zentr.*, 1894, 2, 281. A. Werner and H. Buss, *Ber.*, 1895, **28**, 1280; *J.C.S.*, 1895, **68** (1), 456; *Chem. Zentr.*, 1895, 1, 96.

[29] P. Sabatier and J. B. Senderens, *Compt. rend.*, 1902, **135**, 225; *Chem. Zentr.*, 1902, 2, 636; *J.C.S.*, 1902, **82** (1), 701.

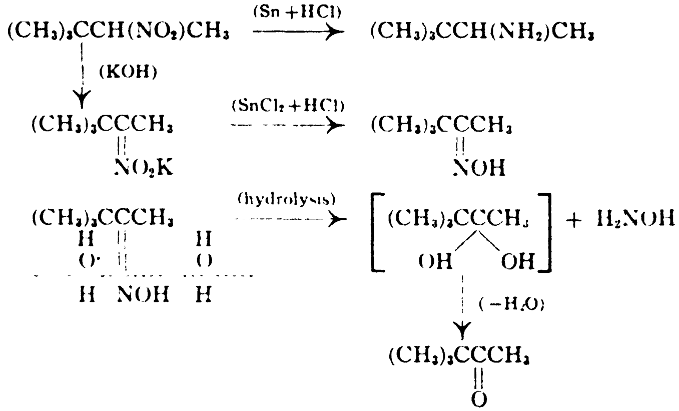
[30] E. Hoffmann and V. Meyer, *Ber.*, 1891, **24**, 3528; *J.C.S.*, 1892, **62**, 291.

[31] V. Meyer, *Ber.*, 1872, **5**, 399; *J.C.S.*, 1872, **25**, 682.

[32] R. A. Worstall, *Am. Chem. J.*, 1898, **20**, 202; 1899, **21**, 218; *J.C.S.*, 1898, **74** (1), 346; 1899, **76** (1), 399.

[33] M. I. Konowalow, *J. Russ. Phys. Chem. Soc.*, 1893, **25**, 389, 472; 1905, **37**, 551; 1906, **38**, 109, 124; *J.C.S.*, 1894, **66** (1), 159, 265; 1905, **88** (1), 764; 1907, **92** (1), 1. *Ber.*, 1895, **28**, 1852; *J.C.S.*, 1895, **68** (1), 633; *Chem. Zentr.*, 1895, 1, 760.

Markownikow[34] found that the reduction of 3-nitro-2,2-dimethylbutane and 3-nitro-2,2-dimethylpentane, with tin and hydrochloric acid, yielded amines, but that the corresponding isonitro compounds (as the alkali salts) added to stannous chloride and hydrochloric acid gave rise to ketones, ketoximes being formed as intermediate products. These reactions are represented by the following example:



$$(CH_3)_3CCH(NO_2)CH_3 \xrightarrow{(Sn+HCl)} (CH_3)_3CCH(NH_2)CH_3$$

$$\downarrow (KOH)$$

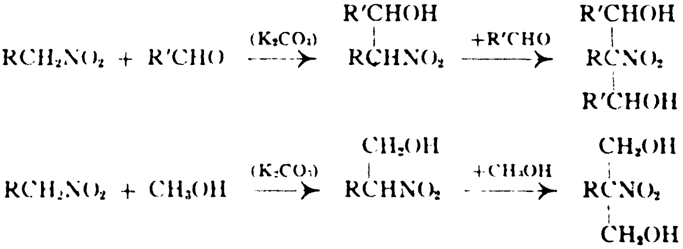
$$(CH_3)_3C\underset{\underset{NO_2K}{\|}}{C}CH_3 \xrightarrow{(SnCl_2+HCl)} (CH_3)_3C\underset{\underset{NOH}{\|}}{C}CH_3$$

$$(CH_3)_3C\underset{\underset{NOH}{\|}}{C}CH_3 + \underset{H}{\overset{H}{O}}\;\underset{H}{\overset{H}{O}} \xrightarrow{(hydrolysis)} \left[(CH_3)_3C\underset{OH\;\;OH}{C}CH_3\right] + H_2NOH$$

$$\xrightarrow{(-H_2O)} (CH_3)_3C\underset{\underset{O}{\|}}{C}CH_3$$

Amines and ketones result from the reduction of the nitro derivatives of the cycloparaffins. Thus, Markownikow[35] reported that nitrocyclohexane is transformed by zinc and glacial acetic acid into cyclohexanone but when the reduction was carried out with tin and hydrochloric acid cyclohexylamine was obtained. Nametkin[36] prepared the corresponding amine from 1-nitro-1-methylcyclohexane and tin and hydrochloric acid. On the other hand, when 3-nitro-1-methylcyclohexane was reduced under similar conditions 3-amino-1-methylcyclohexane and 1-methylcyclohexanone-3 resulted.

Other reactions of primary and secondary nitro compounds are their condensations with aldehydes (aliphatic,[37] aromatic,[38] and chloro-,[39]) and with methyl alcohol.[40] These condensations may be illustrated by the following typical courses of reaction:



$$RCH_2NO_2 + R'CHO \xrightarrow{(K_2CO_3)} R\overset{\overset{R'CHOH}{|}}{C}HNO_2 \xrightarrow{+R'CHO} R\overset{\overset{R'CHOH}{|}}{\underset{\underset{R'CHOH}{|}}{C}}NO_2$$

$$RCH_2NO_2 + CH_3OH \xrightarrow{(K_2CO_3)} R\overset{\overset{CH_2OH}{|}}{C}HNO_2 \xrightarrow{+CH_3OH} R\overset{\overset{CH_2OH}{|}}{\underset{\underset{CH_2OH}{|}}{C}}NO_2$$

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[34] W. B. Markownikow, *Ber.*, 1899, **32**, 1441; 1900, **33**, 1905; *J.C.S.*, 1899, **76** (1), 553; 1900, **78** (1), 469; *Chem. Zentr.*, 1899, **2**, 180; 1900, **2**, 311.

[35] W. B. Markownikow, *Ann.*, 1898, **302**, 1; *Chem. Zentr.*, 1898, **2**, 972; *J.C.S.*, 1899, **76** (1), 22.

[36] S. S. Nametkin, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 691; *J.C.S.*, 1910, **98** (1), 830; *Chem. Zentr.*, 1910, **2**, 1377.

[37] L. Henry, *Compt. rend.*, 1895, **120**, 1265; **121**, 210; *J.C.S.*, 1895, **68**, 637; 1896, **70**, 4; *Chem. Zentr.*, 1895, **1**, 156, 526; *Rec. trav. chim.*, 1897, **16**, 189; *J.C.S.*, 1898, **74**, 4. J. Pauwels, *Rec. trav. chim.*, 1898, **17**, 27; *J.C.S.*, 1898, **74** (1), 506; *Chem. Zentr.*, 1898, **1**, 926.

[38] B. Priebs, *Ber.*, 1883, **16**, 2591; *J.C.S.*, 1884, **46**, 313. *Ann.*, 1884, **225**, 319; *J.C.S.*, 1885, **48**, 160; *Chem. Zentr.*, **1884**, 973. M. Holleman, *Rec. trav. chim.*, 1904, **23**, 283; *J.C.S.*, 1905, **88** (1), 42; *Chem. Zentr.*, 1905, **1**, 89.

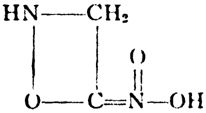
[39] F. D. Chattaway and P. Witherington, *J.C.S.*, **1935**, 1178; *Brit. Chem. Abs.* **A**, 1935, **1224**; *Chem. Abs.*, 1935, **29**, 7377. F. D. Chattaway, J. G. N. Drewitt and G. D. Parkes, *J.C.S.*, **1936**, 1294; *Chem. Abs.*, 1936, **30**, 8149.

[40] J. Pauwels, *Bull. acad. roy. Belgique*, **34** (3), 645; *Chem. Zentr.*, 1898, **1**, 193.

The alkali salts of the nitroparaffins react with halogens,[41] replacing the hydrogen atoms attached to the carbon atom holding the nitro group. By chlorination with hypochlorous acid, nitromethane yields chloropicrin.[42] Primary nitro compounds, when heated with concentrated hydrochloric acid at 150°C. or with phosphoric acid at 100°C., yield the corresponding carboxylic acids.[43] This reaction is shown below:

$$RCH_2NO_2 + HCl + H_2O \longrightarrow RCOOH + HONH_2 \cdot HCl$$

On the other hand, secondary nitropropane[44] is totally decomposed when heated with concentrated hydrochloric acid at 100°C. Fuming sulphuric acid decomposes nitromethane[45] to give carbon monoxide and hydroxylamine but acts on nitroethane[46] to give symmetrical ethane disulphonic acid. Concentrated ammonium hydroxide acts on nitromethane, below 10°C., to give the ammonium salt of methazonic acid.[47] The alkali metal hydroxides act much more vigorously and the reaction is accompanied by considerable decomposition. To methazonic acid has been attributed the structure shown below:



An interesting reaction involving tetranitromethane consists of the introduction of nitro groups into the aromatic nucleus[48] in the presence of pyridine. For example, *m*-nitro-N-dimethyl-*p*-toluidine is formed from N-dimethyl-*p*-toluidine by this treatment. This was the first method used for nitration of the aromatic compounds in an acid-free medium. Reactions of nitroparaffins with diketones,[49] diazo compounds,[50] alkylmagnesium iodides[51] and carbon disulphide[52] have been reported. Taylor and Vesselovsky,[53] in studying the thermal decomposition of nitromethane, found that the main reaction consisted of a unimolecular splitting into nitrosomethane and oxygen. Rice and Rodowskas[54] studied the thermal decomposition of ethyl nitrite, on the other hand, by heating the compound in a furnace under low pressure, and passing the resulting gases over metallic mirrors. Thus, the gases of decomposition were passed over a mirror of tellurium, in several instances. When pure ethyl nitrite was decomposed, the exhaust gases did not attack the mirror. On the other hand, when an inert diluent gas was added, the mirrors were rapidly removed, even when the furnace temperature was no higher than 425°C. The tellurium was found to have been taken up by free methyl radicals, yielding dimethylditelluride, when 1 per cent ethyl nitrite was carried in carbon dioxide.

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[41] J. Tscherniak, *Ann.*, 1876, 180, 123; *J.C.S.*, 1876, 29, 901. A. Hantzsch and H. Kissel, *Ber.*, 1899, 32, 3137; *J.C.S.*, 1900, 78 (1), 89; *Chem. Zentr.*, 1900, 1, 115.

[42] W. D. Ramage, U. S. P. 1,996,388, April 2, 1935, to Great Western Electro-Chemical Co.; *Chem. Abs.*, 1935, 29, 3354.

[43] V. Meyer and J. Locher, *Ann.*, 1876, 180, 163; *J.C.S.*, 1876, 29, 903. A. Geuther, *Ber.*, 1874, 7, 1620; *Chem. Zentr.*, 1875, 98; *J.C.S.*, 1875, 28, 445.

[44] W. R. Dunstan and E. Goulding, *J.C.S.*, 1900, 77, 1262; *Chem. Zentr.*, 1901, 2, 184.

[45] A. Pfungst, *J. pr. Chem.*, 1886, (2) 34, 27; *J.C.S.*, 1886, 50, 862; *Chem. Zentr.*, 1886, 644.

[46] V. Meyer and C. Wurster, *Ber.*, 1873, 6, 1168; *J.C.S.*, 1874, 27, 146; *Chem. Zentr.*, 1873, 727.

[47] W. R. Dunstan and E. Goulding, *loc. cit.*

[48] E. Schmidt and H. Fischer, *Ber.*, 1920, 53, 1529; *Chem. Abs.*, 1921, 15, 86; *J.C.S.*, 1920, 118 (1), 726.

[49] S. Fujise, O. Takeuchi, T. Kamioka and K. Tiba, *Ber.*, 1935, 68, 1272; *Chem. Abs.*, 1935, 29, 6216; *Brit. Chem. Abs.* A, 1935, 1126.

[50] V. Meyer and G. Ambühl, *Ber.*, 1875, 8, 751, 1073; *J.C.S.*, 1875, 28, 1202; 1876, 29, 84; *Chem. Zentr.*, 1875, 486, 678.

[51] J. Bewad, *Ber.*, 1907, 40, 3065; *Chem. Abs.*, 1907, 1, 2469; *Chem. Zentr.*, 1907, 2, 681.

[52] E. Freund, *Ber.*, 1919, 52, 542; *J.C.S.*, 1919, 116, 309; *Chem. Abs.*, 1919, 13, 2526.

[53] H. A. Taylor and V. V. Vesselovsky, *J. Phys. Chem.*, 1935, 39, 1095; *Chem. Abs.*, 1936, 30, 364. See also E. W. R. Steacie and D. S. Calder, *J. Chem. Physics*, 1936, 4, 96; *Chem. Abs.*, 1936, 30, 2088.

[54] F. O. Rice and E. L. Rodowskas, *J.A.C.S.*, 1935, 57, 350; *Chem. Abs.*, 1935, 29, 1772; *Brit. Chem. Abs.* A, 1935, 471.

The investigators believe the reactions involved proceed as follows:

$$(1) \qquad CH_3CH_2ONO \longrightarrow NO + CH_3CH_2O—$$

yielding the free radicle $CH_3CH_2O—$ and the stable molecule NO. This primary decomposition then is followed by:

$$(2) \qquad CH_3CH_2O- \longrightarrow HCHO + CH_3—$$
$$(3) \qquad CH_3- + CH_3CH_2ONO \longrightarrow CH_4 + CH_3CH(ONO)—$$
$$(4) \qquad CH_3CH(ONO)- \longrightarrow NO + CH_3CHO$$

The fact that pure ethyl nitrite did not remove the metallic mirrors was accounted for on this basis by the presumption that reactions (1) and (2) occur in the furnace, and are immediately followed by reactions (3) and (4), thus destroying the free methyl groups before the mirrors were reached. Diluting the ethyl nitrite, then, would reduce the rate of reaction (3), the only bi-molecular reaction of the series, and permit the methyl groups to exist until the mirror was reached. Since the experiment with the tellurium mirror yielded pure dimethylditelluride, it seems probable that only the methyl free-radicals escaped the furnace.

Hass and co-workers,[55] reporting on the toxicity of a sample of nitrated propane (containing also nitromethane and nitroethane in addition to the two nitropropanes), state that its vapors are less toxic than the vapors of benzene, aniline, carbon disulphide, carbon tetrachloride or nitrobenzene.

NITRO COMPOUNDS OF PETROLEUM AND THEIR APPLICATIONS

The increasing use of the Diesel engine has been accompanied by the desire to produce lower-igniting and faster-burning fuels. Although this can be influenced to a considerable extent by selecting fuels of the desired composition, nevertheless extraneous substances have also been added which often cause marked changes in the ignition characteristics of a fuel. Such substances are usually explosive or easily ignitable at relatively low (engine) temperatures. They are generally employed in concentrations of less than 5 per cent in most fuels, and, by means of their explosions or low-temperature ignitions, are able to more completely disperse the injected fuel spray and furnish additional heat which aids in the combustion of the fuel charge. These substances are often referred to as ignition-temperature depressants, or accelerators, or promoters, and impart better ignition qualities to fuels. They are also said to suppress detonation and to decrease delay in inflammation.[56]

The substances which have been used or suggested as ignition promoters include the low molecular weight aliphatic nitro compounds and alkyl nitrites,[57] the alkyl nitrates[58] and the latter mixed with organic peroxides.[59]

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[55] H. B. Hass, E. B. Hodge and B. M. Vanderbilt, *Ind. Eng. Chem.*, 1936, **28**, 339; *Chem. Abs.*, 1936, **30**, 2918.

[56] M. Aubert, P. Clerget and R. Duchene, *Compt. rend.*, 1935, **201**, 879; *Brit. Chem. Abs.* B, 1936, 133.

[57] N. E. Loomis, U. S. P. 1,820,983, Sept. 1, 1931, to Standard Oil Development Co.; *Chem. Abs.*, 1931, **25**, 5980; *Brit. Chem. Abs.* B, 1932, 636. F. Hofmann and K. Gieseler, German P. 574,678, 1933; *Chem. Abs.*, 1933, **27**, 4666.

[58] C. J. Sims, British P. 294,129, 1927; *Chem. Abs.*, 1929, **23**, 2020; *Brit. Chem. Abs.* B, 1928, 703. W. Helmore, British P. 366,947, 1930; *Brit. Chem. Abs.* B, 1932, 378. Imperial Chemical Industries Ltd., French P. 730,238, 1932; *Chem. Abs.*, 1933, **27**, 401. D. T. Jones, British P. 374,481, 1932, to Imperial Chemical Industries Ltd.; *Chem. Abs.*, 1933, **27**, 4070; *Brit. Chem. Abs.* B, 1932, 827. R. Stansfield, *Proc. World Petr. Congr.*, 1933, **2**, 256; *Brit. Chem. Abs.* B, 1934, 949; *Chem. Abs.*, 1934, **28**, 3867. M. E. Weber and J. Spiltor, Belgium P. 405,078, 1934; *Chem. Abs.*, 1935, **29**, 3497.

[59] W. Helmore, British P. 354,398, 1931; *Brit. Chem. Abs.* B, 1931, 1002; *Chem. Abs.*, 1932, **26**, 2851; British P. 352,550, 1931; *Chem. Abs.*, 1932, **26**, 3906; U. S. P. 1,849,051, March 8, 1932;

Salzberg and Peterson[60] have suggested the use of compounds of the type RR′NN:O, in which R and R′ are alkyl radicals. Thus dibutyl- or di-methyl-nitrosoamine may be used. Besides being used in hydrocarbon fuels, the alkyl nitrates have been added to alcohol fuels,[61] in amounts less than 1 per cent, to improve their burning properties. Griffith and Hill[62] have suggested substances which contain halogen atoms and nitrate groups on adjacent carbon atoms, the nitrate of 9,10-bromohydroxystearic acid being an example.

Some investigators, however, have subjected fuels to nitrating treatments instead of adding extraneous substances to promote ignition. Wingett[63] distilled a fuel, under a pressure of 300 pounds per square inch, in the presence of a small quantity of a mixture of sulphuric and nitric acids. The resulting material was said to be more sensitive to low temperature ignition than before nitration. Grevel[64] treated a gas oil (boiling range 270-360°C., sp. gr. 0.80-0.87) with nitric acid (expediently with fuming nitric acid) and, after the conclusion of gas evolution, neutralized the unused acid with sodium bicarbonate. This oil, either alone or mixed with other petroleum fractions, was suggested as a motor fuel, presumably for motors equipped with spark or similar ignition means and hence not relying on compression to cause ignition. By distillation (with steam or under reduced pressure) decolorization of the nitrated oil was accomplished.

Winand[65] describes a fuel designed especially for submarine engines, which must operate without direct access to the atmosphere. This fuel consists of a mixture of tetranitroethane and mono-, di-, or trinitrobenzol, without the addition of hydrocarbon material. Nitromethane has been employed for the removal of carbon deposits from internal combustion engines.[66] A mixture consisting of nitromethane, benzol and ethyl alcohol is injected into the cylinders which have been previously heated to 150°F. After remaining for 2 hours the engine is started and the carbon blown out the exhaust. Hass and co-workers[67] investigated the possibility of using the nitropropanes and nitrobutanes as lacquer solvents. They found that, when dissolved in an alcohol such as 1-butanol, these nitro compounds possessed dilution ratios equal or superior to those of the ester solvents (butyl and amyl acetates) and that lacquers containing these compounds exhibited good blush resistance. They further report that tests indicate the nitroparaffins possess possible value in the solvent refining of lubricating oils. Fitch[68] has described the production of a resinous substance from olefin material and sulphur dioxide which is soluble in nitromethane.[69] The solution prepared in this way is said to contain a high percentage of solids, and to possess a high viscosity.

Drinberg and associates[70] produced varnish resins by nitrating paraffin oil,

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Chem. Abs., 1932, **26**, 4466, all to Imperial Chemical Industries Ltd. British P. 428,972, 1935; *Brit. Chem. Abs.* **B**, 1935, 713; *Chem. Abs.*, 1935, **29**, 7055; German P. 617,429, 1935; *Chem. Abs.*, 1935, **29**, 8294; both to Bataafsche Petroleum Maatschappij.

[60] P. L. Salzberg and W. R. Peterson, U. S. P. 2,009,818, July 30, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, **29**, 6405.

[61] J. Penhale, British P. 178,373, 1922; *Chem. Abs.*, 1922, **16**, 3195.

[62] R. H. Griffith and S. G. Hill, British P. 436,027, 1935; *Chem. Abs.*, 1936, **30**, 1980; *Brit. Chem. Abs.* **B**, 1935, 1083.

[63] J. N. Wingett, U. S. P. 1,185,747, June 6, 1916, to W. A. Haggott; *J.S.C.I.*, 1916, **35**, 828.

[64] A. Grevel, German P. 379,966, 1923; *J.S.C.I.*, 1923, **42**, 1166*A*.

[65] P. Winand, U. S. P. 914,624, March 9, 1909; *Chem. Abs.*, 1909, **3**, 1690; *J.S.C.I.*, 1909, **28**, 787.

[66] W. G. Lovell and T. A. Boyd, U. S. P. 1,825,358, September 29, 1931, to General Motors Research Corp.; *Chem. Abs.*, 1932, **26**, 284; *Brit. Chem. Abs.* **B**, 1932, 586.

[67] H. B. Hass, E. B. Hodge and B. M. Vanderbilt, *Ind. Eng. Chem.*, 1936, **28**, 339; *Chem. Abs.*, 1936, **30**, 2918.

[68] L. H. Fitch, U. S. P. 2,045,592, June 30, 1936, to Phillips Petroleum Co.; *Chem. Abs.*, 1936, **30**, 5683.

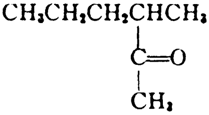
[69] See Chapter 25.

[70] A. Y. Drinberg, A. A. Blagonravova and E. M. Prik, *J. Applied Chem. (U.S.S.R.)*, 1934, **7**, 1223; *Chem. Abs.*, 1935, **29**, 5540.

petrolatum, and gas oil with 30°Bé nitric acid, both alone and mixed with 73°Bé sulphuric acid at temperatures of 120°, 130° and 200°C. Such resins were soluble in acetone, amyl acetate, benzene and chloroform, and yielded transparent films on evaporation of their solutions. A brownish resin was obtained from the unsaturated compounds of petroleum and fuming nitric acid. In preparing tar emulsions for use in paving compositions, Daimler[71] used "humic acids" as emulsifying agents. These acids were made by the nitration of coal or pitches and were soluble in alkalies, giving brown solutions. Nitrated petroleum fractions have also been used as dyes, plasticizers and as intermediates in the production of motor fuels.[72]

APPLICATIONS OF FRIEDEL-CRAFTS REACTION TO PARAFFIN AND CYCLOPARAFFIN HYDROCARBONS

Hopff[73] obtained a ketone by the action of acetyl chloride on pentane in the presence of aluminum chloride to which he assigned the structure corresponding to 2-acetylpentane,



$$CH_3CH_2CH_2\underset{\substack{|\\ C=O\\ |\\ CH_3}}{C}HCH_3$$

Later, however, Nenitzescu and Chicos[74] showed, by oxidizing this substance to the corresponding acid, that it was actually 2-acetyl-3-methylbutane. Hence, they postulated the following mechanism:

$$n\text{-}C_5H_{12} \xrightarrow{(AlCl_3)} (CH_3)_2CHCH_2CH_3 \xrightarrow{-H_2} (CH_3)_2C{=}CHCH_3$$

$$\xrightarrow{+CH_3COCl} (CH_3)_2C(Cl)CH(CH_3CO)CH_3 \xrightarrow{+H_2} (CH_3)_2CHCH(CH_3CO)CH_3$$

Similarly, the ketone $(CH_3)_2CHCH(CH_3CO)CH_2CH_3$ was obtained from *n*-hexane. On the other hand, Zelinskii and Leder-Packendorff[75] treated a naphtha benzine, corresponding to the formula C_6H_{14}, with acetyl chloride and aluminum chloride and obtained a 22.5 per cent yield of a ketone mixture which they showed consisted of 1-methyl-2-acetylcyclopentane and 1-methyl-3-acetylcyclopentane. In this work they proved also that 2-methylpentane was not the origin of the ketones formed since it failed to react with acetyl chloride in the presence of aluminum chloride.

Carbon monoxide may be condensed with the paraffins in the presence of aluminum chloride, but whereas the aromatic hydrocarbons condense with carbon monoxide to yield aldehydes, the paraffins in this reaction yield ketones. A study of this reaction led Hopff and Nenitzescu[76] to suggest that the reaction between *n*-butane and carbon monoxide proceeds as follows:

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[71] K. Daimler, U. S. P. 2,008,978, July 23, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 6016.

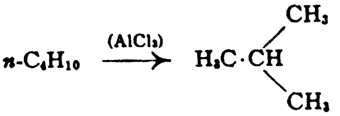
[72] Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934.

[73] H. Hopff, *Ber.*, 1931, **64**, 2739; *Chem. Abs.*, 1932, **26**, 1236; *Brit. Chem. Abs.*, **A**, 1932, 44.

[74] C. D. Nenitzescu and I. Chicos, *Ber.*, 1935, **68**, 1584; *Chem. Abs.*, 1935, **29**, 7279; *Brit. Chem. Abs.* **A**, 1935, 1221.

[75] N. D. Zelinskii and L. Leder-Packendorff, *Ann.*, 1935, **518**, 260; *Chem. Abs.*, 1935, **29**, 6401; *Brit. Chem. Abs.* **B**, 1935, 836.

[76] H. Hopff and C. D. Nenitzescu, *Angew. Chemie*, 1936, **49**, No. 13, 553. H. Hopff, C. D. Nenitzescu, D. A. Isacescu and I. P. Cantuniari, *Ber.*, 1936, **69**, 2244; *Chem. Abs.*, 1937, **31**, 366.

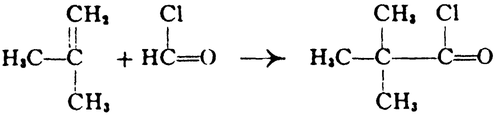


(rearrangement giving mixture of butanes)

$C_4H_{10} \longrightarrow C_4H_8 + H_2$ (mixed butanes dehydrogenated)

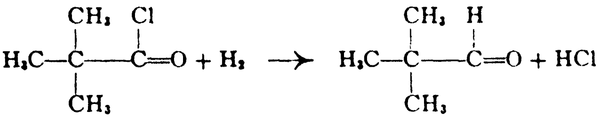
$$CO + HCl \xrightarrow{(AlCl_3)} \left[HCOCl\right]$$

Carbon monoxide (as formyl chloride) adds to the unsaturated compounds to produce from isobutene, trimethylacetyl chloride:



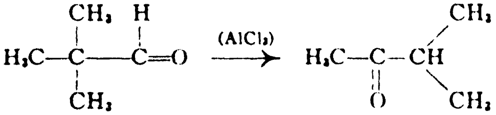
$$H_3C{-}\begin{array}{c}CH_2\\ \|\\ C\\ |\\ CH_3\end{array} + H\begin{array}{c}Cl\\ |\\ C\end{array}{=}O \longrightarrow H_3C{-}\begin{array}{c}CH_3\\ |\\ C\\ |\\ CH_3\end{array}{-}\begin{array}{c}Cl\\ |\\ C\end{array}{=}O$$

This product is reduced by hydrogen (arising from the dehydrogenation) to trimethylacetaldehyde:

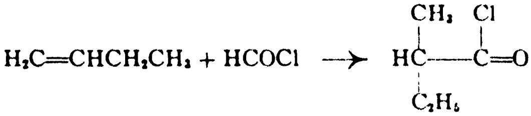


$$H_3C{-}\begin{array}{c}CH_3\\ |\\ C\\ |\\ CH_3\end{array}{-}\begin{array}{c}Cl\\ |\\ C\end{array}{=}O + H_2 \longrightarrow H_3C{-}\begin{array}{c}CH_3\\ |\\ C\\ |\\ CH_3\end{array}{-}\begin{array}{c}H\\ |\\ C\end{array}{=}O + HCl$$

Under the influence of aluminum chloride, rearrangement takes place yielding methylisopropylketone:

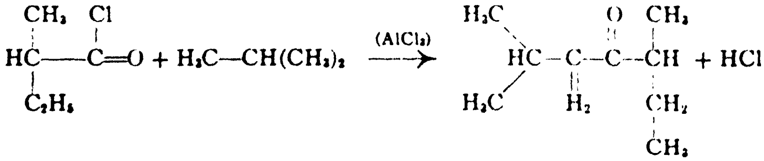


while from *n*-butene and formyl chloride, methylethylacetyl chloride is formed:



$$H_2C{=}CHCH_2CH_3 + HCOCl \longrightarrow H\begin{array}{c}CH_3\\ |\\ C\\ |\\ C_2H_5\end{array}{-}\begin{array}{c}Cl\\ |\\ C\end{array}{=}O$$

This in turn reacts with unchanged isobutane to yield isobutyl-*sec*-butyl ketone:



By interaction of the various products present in the reaction mixture, there arise, in addition to the principal product of the interaction of carbon monoxide and *n*-butane, isobutyl-*sec*-butyl ketone, a complex mixture of methylethylacetic acid, trimethylacetic acid, and *ter*-butyl-isopropyl ketone.

Cyclohexane, in the presence of aluminum chloride, undergoes a primary isomerization to methylcyclopentane which then loses hydrogen and adds acetyl chloride to form a chloroketone.[77] The latter is simultaneously hydrogenated to give

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[77] C. D. Nenitzescu and G. G. Vantu, *Bull. soc. chim.*, 1935, (5) 2, 2209; *Chem. Abs.*, 1936, 30, 1749.

1-methyl-2-acetylcyclopentane. This isomerization of cyclohexane to methylcyclopentane, according to Nenitzescu and Cantuniari,[78] is not due, however, to the smaller strain of the cyclopentane ring because the strain-free cyclohexane ring appears to be the more stable. No acetylcyclohexane is formed in this reaction. Cyclohexene,[79] on the other hand, gives acetylcyclohexane (methyl cyclohexyl ketone) when treated with acetyl chloride and aluminum chloride in carbon disulphide at −20°C.

Paraffin hydrocarbons have also been shown to react, in the presence of aluminum chloride, with phthalic anhydride to form keto-acids, with ethylene oxide to produce alcohols, and with phosgene and hydrogen to give aldehydes and ketones.[80]

OTHER REACTIONS OF THE PARAFFINS AND CYCLOPARAFFINS

Looker, Kester, Hass and Friend[81] studied the action of nitrosyl chloride (NOCl) on the paraffin hydrocarbons, both in the presence and in the absence of light, and obtained a number of products. The reactions were carried out in the liquid and also in the gaseous phases, and at elevated temperatures and pressures. Since not only nitrosyl chloride but also the products of reaction were very corrosive, the apparatus used was lined with tantalum. Both gaseous and liquid paraffins were suitable as the hydrocarbon materials. In the case of the action of nitrosyl chloride on butane three types of reactions occurred: (1) chlorination, giving mono- and polychlorides with the latter predominating; (2) oxidation, giving fatty acids, including butyric, propionic, acetic and formic acids; and (3) nitrosation, which resulted in the formation of oximes. Nitrosyl chloride mixed with butane produces a slow evolution of gas which finally results in 2 layers, the lower one being miscible, and the upper one immiscible, with water. After the reaction is complete, as indicated by the disappearance of the reddish color (due to unreacted nitrosyl chloride), the mixture is refluxed with the strong hydrochloric acid formed during the reaction so as to hydrolyze the oximes to aldehydes and ketones, and the nitriles to fatty acids. Following hydrolysis, the water-miscible layer is fractionally distilled to give methyl ethyl ketone, acetic acid, propionic acid and butyric acid. A residue composed of ammonium chloride and hydroxylamine hydrochloride remains. The water-immiscible layer is fractionally distilled to give 1-chlorobutane, 2-chlorobutane, 1,1-dichlorobutane, 2,-2-dichlorobutane and other polychlorobutanes. Certain lachrimatory substances are also formed which are thought to be chlorinated ketones.

That light has a strong influence on the course of the reaction between nitrosyl chloride and paraffins has been substantiated by the work of Mitchell and Carson[82] on the color changes ensuing during the reaction between *n*-hexane and nitrosyl chloride. In bright sunlight, the two compounds react to yield a brown oil, which, on steam distillation, yields about equal proportions of methyl-*n*-butyl ketone and methyl-*n*-propyl ketone. When the reaction was carried out in the absence of bright sunlight, a blue color developed slowly, then gradually disappeared, but very little of the oil as from the first experiment was obtained. An absorption-spectrum study of this reaction mixture showed that there were very powerful absorption bands in the violet and ultraviolet, and also bands located in the blue and orange (headed at 4780 Å and 6000 Å respectively). On removing the hydrogen chloride and nitrosyl chloride from one of the blue solutions (by blowing nitrogen through it) it was found that a strong absorption band existed in the red, headed at about 6600 Å. The reaction was then carried on in tubes immersed in cylinders of copper sulphate solution, which served as filters to remove the red rays from light passing through them, and the apparatus exposed to sunlight. Under these conditions, the reaction was arrested at the blue stage, and little oil was formed. When the evolution of hydrogen chloride ceased, the solutions were again saturated with nitrosyl chloride and exposed. This operation was repeated three successive times, and the resulting blue solutions washed with dilute sodium bicarbonate solution, dried, and fractionated under reduced pressure. The blue liquid concentrated in this way, was found to constitute only a few cubic centimeters in each liter of hexane reacted. Analytical data indicated that this liquid, which was quite stable when kept in the dark, consisted of 2,2-chloronitrosohexane and 3,3-chloronitrosohexane.

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[78] C. D. Nenitzescu and J. P. Cantuniari, *Ber.*, 1933, **66**, 1097; *Brit. Chem. Abs.* **A**, 1933, 941; *Chem. Abs.*, 1933, **27**, 4780.

[79] C. D. Nenitzescu and J. P. Cantuniari, *Ann.*, 1934, **510**, 269; *Chem. Abs.*, 1934, **28**, 5413; *Brit. Chem. Abs.* **A**, 1934, 773.

[80] See, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

[81] C. D. Looker, E. B. Kester, H. B. Hass and W. Z. Friend, U. S. P. 1,923,630, August 22, 1933, to The Baltimore Gas Engineering Corp.; *Chem. Abs.*, 1933, **27**, 5337; *Brit. Chem. Abs.* **B**, 1934, 533. Also, private communication from E. B. Kester.

[82] S. Mitchell, and S. C. Carson, *J.C.S.* **1936**, 1005; *Brit. Chem. Abs.* **A**, 1936, 1090; *Chem. Abs.*, 1936, **30**, 6703.

Lelgemann[83] produced a gasoline substitute from high boiling paraffin material by reacting the latter with nitrosyl chloride at temperatures between 120° and 370°C. in the presence of iron and aluminum chlorides. About 4 to 5 ounces of nitrosyl chloride and 5 to 12 pounds of a mixture of equal parts of the metallic chlorides were used with each 100 pounds of charging stock. The hydrocarbon charge was heated to the temperature of incipient cracking and the nitrosyl chloride introduced at that point.

Rice[84] prepared lead alkyls from paraffins by heating the latter to 500-1000°C. at sub-atmospheric pressures and passing the products over finely divided lead, after which they were rapidly cooled to −80°C. and finally to −190°C. to separate the lead alkyls thus formed. Heptane, for example, gave mainly the methyl and ethyl derivatives when treated in this manner. Nenitzescu and Isacescu[85] investigated the behavior of cyclohexane toward inorganic halides in the presence of aluminum chloride at 65-70°C. Arsenic trichloride, silicon tetrachloride, stannic chloride, sulphur monochloride, thionyl chloride and sulphuryl chloride all converted cyclohexane into bicyclohexyl. Phosphorus trichloride gave unsaturated compounds, whereas mercuric chloride, silver chloride, chromyl chloride and phosphorus oxychloride did not react. Candea and Murgulescu[86] studied the action of metallic halides on methane at much higher temperatures. At 900°C. a 90 per cent yield of hydrochloric acid was obtained from calcium chloride and methane, while at 700° and 1000° C. the yield was 60 per cent. Also, by careful regulation of the conditions, they obtained 60 per cent yields of hydrochloric acid from sodium chloride and methane. Reactions of the saturated hydrocarbons with sulphur, sulphur monochloride, antimony chloride ($SbCl_5$), chlorosulphonic acid and chromyl chloride have also been reported.[87]

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[83] W. Lelgemann, U. S. P. 1,936,633, November 28, 1933; *Chem. Abs.*, 1934, **28**, 1516; *Brit. Chem. Abs.* **B**, 1934, 823.

[84] F. O. Rice, British P. 407,036, 1932; *Brit. Chem. Abs.* **B**, 1934, 444; *Chem. Abs.*, 1934, **28**, 4847.

[85] C. D. Nenitzescu and D. A. Isacescu, *Ber.*, 1934, 67, 1391; *Chem. Abs.*, 1934, **28**, 7251; *Brit. Chem. Abs.* **A**, 1934, 995.

[86] C. Candea and I. G. Murgulescu, *Chimie et industrie*, 1935, **33**, 800; *Chem. Abs.*, 1935, **29**, 5226; *Brit. Chem. Abs.* **B**, 1935, 534; *14me Congr. chim. ind.*, Paris, 1934, 8; *Chem. Abs.*, 1935, **29**, 6369.

[87] See, Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934.

Chapter 48

Naphthenic Acids

Oxygen-containing compounds comprise only a small fraction of the constituents of mineral oils and are reported to be of two types, namely, phenolic bodies, such as cresols, xylenols, or di- and triethylphenol, and naphthenic acids.[1] The latter, present in the larger proportion, are the carboxylic derivatives of cycloparaffin hydrocarbons and have found technical applications, particularly in the form of their alkali and heavy-metal salts. Although naphthenic acids occur to some extent in practically all crude petroleums, or their distillates, the chief sources are Russian, Rumanian and, to a lesser degree, Polish oils, the German and American crudes yielding comparatively small quantities. Schmitz[1a] states that the acidity of certain crude oils in the region of Apsheron (Russia) is:

	Acidity, %[a]
Balakhanui light oil	0.08-0.16
Balakhanui heavy oil	0.20
Sabountschy	0.10-0.20
Bibi-Eybat	0.07-0.16
Ramany	0.08-0.18

[a] Analyses made in 1933 and 1934.

The content of naphthenic acids is frequently not greater than 2 per cent and is often less than 0.1 per cent, but even on the basis of 0.1 per cent the potential world-annual production is estimated at 200,000,000 kg. or approximately 50,000 tons.

The proportions of naphthenic acids in various fractions of a Balakhanui lubricating oil distillate and a heavy Balakhanui crude oil, as reported by Blagovidov and Terteryan,[2] are indicated in Table 205.

TABLE 205.—*Proportions of Naphthenic Acids in Balakhanui Oil.*

	% Naphthenic Acids	
Fraction	Lubricating Distillate	Heavy Crude
Kerosene	0.83	0.69
Light gas oil	1.54	1.60
Heavy gas oil	1.65	2.48
Spindle oil	1.57	2.98
Machine oil	1.16	2.68
Cylinder oil	0.82	1.90

Gas oils from Texas and California petroleums are reported to contain 0.35-0.36 per cent acids, and some Louisiana and Gulf Coast crudes as high as 0.67-0.70 per cent.[3] According to Goldberg and Ter-Akopova,[4] determination of acidic constituents should be made by extraction with alcoholic sodium or potassium hydroxide as results obtained with aqueous solutions of alkali are likely to be unreliable because of the formation of emulsions.

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[1] J. v. Braun, *Chem.-Ztg.*, 1935, **59**, 485; *Chem. Abs.*, 1935, **29**, 5429; *Brit. Chem. Abs.* **B**, 1935, 618; *J. Inst. Pet. Tech.*, 1935, **21**, 298A. See also, E. Schmitz, *Mat. Grasses*, 1919, **12** (140), 5273. Also, *Chem. Trades J.*, 1935, **96**, 487; *J. Inst. Pet. Tech.*, 1935, **21**, 299A.

[1a] E. Schmitz, *private communication.*

[2] I. F. Blagovidov and A. B. Terteryan, *Azer. Neft. Khoz.*, **1933**, No. 11-12, 128; *Chem. Abs.*, 1934, **28**, 7491. For a discussion of the constitution and properties of naphthenic acids, see E. Schmitz, *Kunststoffe*, 1914, **4**, 50; *Chem. Abs.*, 1914, **8**, 1341.

Examination of some commercial naphthenic acids from the alkali wash of a West Texas (U.S.A.) pressure distillate was made by Williams and Richter.[5] These investigators found that the acidic constituents consisted for the most part of phenolic compounds, phenol, *o*-, *m*-, and *p*-cresol, 1,3,5-xylenol, and 1,4,2-xylenol. Some ethyl mercaptan was also present. In addition, the following aliphatic acids were isolated; isovaleric, *n*-heptylic, *n*-octylic, and *n*-nonylic. These results seemed to indicate that cyclic carboxylic acids are not present exclusively as many of the earlier workers believed. A study of the mixed acids from a Texas oil was made by Cosciug,[6] who attempted to separate them according to the method of v. Braun and Wittmeyer.[7] Only a very small quantity of one acid, having the formula $C_8H_{14}O_2$ and boiling at 138-142°C. (12 mm.), was secured. The major portion of the acidic bodies, however, appeared to be derivatives of the isomeric hydrocarbons whose constitutions corresponded to $C_{10}H_{18}$.

Although the formation of naphthenic acids in petroleum distillates has been attributed largely to oxidation (by air-blowing) during the alkaline wash of refinery operations, nevertheless some results obtained by v. Braun and Wittmeyer[8] show that these acids pre-exist in the crude oil. A fraction (boiling 180-260°C.) was extracted with liquid sulphur dioxide and the soluble and insoluble portions separated and subjected to an alkaline wash. If the acids were due only to oxidation during this latter operation, then different products should be obtained from the two portions. v. Braun and Wittmeyer found, however, that three times as great a quantity of acids were extracted from the sulphur dioxide-soluble portion as from the other. Even though it was impossible to isolate individual acids, nevertheless comparisons of mixtures of the same boiling range and of their degradation products by the amine-olefin or the progressive degradation method[9] indicated their similarity in properties and constitution. These investigators concluded, therefore, that naphthenic acids were present in the crude distillate prior to oxidation. Attempts to separate the acids into closely related substances by extraction with liquid sulphur dioxide at —10° to —20°C. were not successful.

EXTRACTION OF NAPHTHENIC ACIDS FROM PETROLEUM

Extraction of crude petroleum oils or distillates with alkali usually affords the largest yields of naphthenic acids. Loss of acids may result from the partial refining of distillates or still bottoms, destruction during distillation, unsatisfactory treating procedures, or partial transfer to acid sludge when sulphuric acid is employed as the refining agent.[10] Methods for the recovery of naphthenic acids appear to be of two general types:[11] (1) treatment of the oil with aqueous alkali at elevated temperatures, acidifying the solution, extracting with a low-boiling distillate, and separating acids and distillate by fractional distillation. (2) The oil is distilled in the presence of an alkali, for example, calcium or sodium oxide,[12] and the resulting soaps freed from hydrocarbons by extraction with 80 per cent alcohol, the soaps being soluble in this solvent. Further purification may be effected by aeration of the acids in the presence of cobalt naphthenate.

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[3] V. L. Shipp, *Oil Gas J.*, 1936, 34 (44), 56; *Chem. Abs.*, 1936, 30, 5401; *J. Inst. Pet. Tech.*, 1936, 22, 367A.

[4] D. Goldberg and M. Ter-Akopova, *Azer. Neft. Khoz.*, 1933, No. 10, 76; *Chem. Abs.*, 1934, 28, 7491.

[5] M. Williams and G. H. Richter, *J.A.C.S.*, 1935, 57, 1686; *Brit. Chem. Abs.* B, 1935, 1081; *Chem. Abs.*, 1935, 29, 7629; *J. Inst. Pet. Tech.*, 1935, 21, 407A.

[6] T. Cosciug, *Ann. sci. univ. Jassy*, 1935, 20, 341; *Chem. Abs.*, 1936, 30, 2733.

[7] J. v. Braun and H. Wittmeyer, *Ber.*, 1934, 67, 1739; *Chem. Abs.*, 1935, 29, 585; *Brit. Chem. Abs.* A, 1934, 1359.

[8] J. v. Braun and H. Wittmeyer, *Ber.*, 1934, 67, 1739; *Chem. Abs.*, 1935, 29, 585; *Brit. Chem. Abs.* A, 1934, 1359.

[9] For a review of these methods, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

[10] D. Goldberg, E. Shaverdova and V. Masumyan, *Azer. Neft. Khoz.*, 1934, No. 2, 72; *Chem. Abs.*, 1934, 28, 7493. See also, B. Ruibak and E. Alfimova, *Azer. Neft. Khoz.*, 1934, No. 10-11, 100; *Chem. Abs.*, 1935, 29, 7630. For a method of analysis of alkali sludge, see B. M. Ruibak, *Azer. Neft. Khoz.*, 1935, No. 4, 84; *Brit. Chem. Abs.* B, 1936, 819; *Chem. Abs.*, 1935, 29, 6745.

Washing crude Baku lubricating oil distillates at 60-70°C. with 4 per cent aqueous sodium hydroxide is reported to effect as high as 96.7 per cent neutralization.[13] The alkali sludge so obtained was black in color and contained about 36.8 per cent unsaponifiable material. The treated oil, however, yielded a higher proportion of ash than the untreated. Crude oils having 0.9 to 1.2 per cent petroleum acids can be washed with alkali in like manner, though the addition of 1 per cent of kerosene naphthenic acids may be required to break the emulsions which are formed. Also, it has been pointed out that the removal of naphthenic acids from a residual oil stock and the separation of the latter into distillate fractions may be accomplished in a one-stage operation.[14] A concentrated aqueous solution of sodium hydroxide is incorporated in the oil and the mixture is conducted through a heating coil at about 400°C. In order to maintain the substances in the liquid phase the heating is effected at high pressures. The heated mixture is then led rapidly into the center of a fractionating column, the latter being kept under a high vacuum. The oil which remains unvaporized flows to the lower portion of the fractionating column and is distilled by further heating. Vaporized oil in the center of the column is fractionated to condense a lubricant cut which may be removed as a side stream. Tarry matter, naphthenic acids and caustic soda are removed at the bottom of the column. Alkali sludge from crude oil often contained 50-60 per cent of oil or unsaponifiable matter. Analysis of the organic portion of such sludge (from Bibi-Eibat crude oil) indicated its composition to be 0.23 per cent asphaltogenic acids, 63.52 per cent naphthenic acids, 0.96 per cent asphaltenes, 4.07 per cent resins, and 31.16 per cent oil. The removal of unsaponifiable matter from alkaline sludge is said to be effected by extracting the sludge with a gasoline boiling at 325°C. (end point).[15] Countercurrent operation is said to result in smaller loss of oil and higher yields of acids are secured if the alkali wash precedes refining with sulphuric acid. The use of 10 per cent aqueous calcium chloride for breaking oil and alkali emulsions is suggested by Robinson.[16]

The following procedure is recommended by Gelbke:[17] Waste alkali (from refining mineral oils) is dehydrated and lixiviated with dry acetone and the extract is cooled and allowed to stand until clear. Afterwards the solvent is removed from the clear solution by evaporation.

Removal of naphthenic acids and phenols may be accomplished by bringing a mixture of steam and oil vapors in contact with a hot aqueous solution of sodium hydroxide.[18] The temperature and concentration of the latter are such that an appreciable quantity of steam is neither evolved nor absorbed during the extraction step. The apparatus consists of a steel shell in which are placed trays. The latter contain vapor jets covered by bells to insure an adequate time of contact between the oil vapors and caustic soda solution. In the procedure gaseous oil and water are bubbled through the caustic soda solution to extract the naphthenic acids

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[11] Y. Mayor. *Chimie et industrie*, 1935, **34**, 526; *J. Inst. Pet. Tech.*, 1936, **22**, 28A; *Brit. Chem. Abs.* B, 1935, 1036; *Chem. Abs.*, 1935, **29**, 7967. See also, V. E. Parkhomenko. *Neft*, 1932, **3** (7), 14; *Chem. Abs.*, 1936, **30**, 3976.

[12] In commercial operations sodium hydroxide is often employed. The use of sodium carbonate is described by R. S. Prozumentik and G. K. Izmailov, *Azer. Neft. Khoz.*, **1934**, No. 3, 8; *Chem. Abs.*, 1934, **28**, 7506.

[13] A. S. Velikovskii and A. V. Druzhinina. *Neft. Khoz.*, 1933, **25**, 48; *Chem. Abs.*, 1934, **28**, 301; *Brit. Chem. Abs.* B, 1934, 308. See also. A. B. Terteryan and I. F. Blagovidov, *Azer. Neft. Khoz.*, **1933**, No. 4, 46; *Chem. Abs.*, 1934, **28**, 7492. B. M. Erlikh, *Neft*, 1935, **6** (5), 22; *J. Inst. Pet. Tech.*, 1936, **22**, 366A; *Chem. Abs.*, 1936, **30**, 3981. *Cf.* A. V. Druzhinina and V. T. Brazhnikov, *Neft. Khoz.*, 1935, **29**, No. 9, 47; *Chem. Abs.*, 1936, **30**, 8585.

[14] W. B. Logan. U. S. P. 1,998,765, April 23, 1935, to Texas Co.; *Chem. Abs.*, 1935, **29**, 3823; *Brit. Chem. Abs.* B, 1936, 358.

[15] J. T. Rutherford, Canadian P. 357,654 and 357,655, 1936, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 4312.

[16] J. Robinson, U. S. P. 1,984,432, Dec. 18, 1934, to Standard Oil Co. of Ind.; *Brit. Chem. Abs.* B, 1935, 1127; *Chem. Abs.*, 1935, **29**, 916.

[17] M. Gelbke, German P. 595,987, 1934, to Sudfeldt & Co.; *Chem. Abs.*, 1934, **28**, 5191.

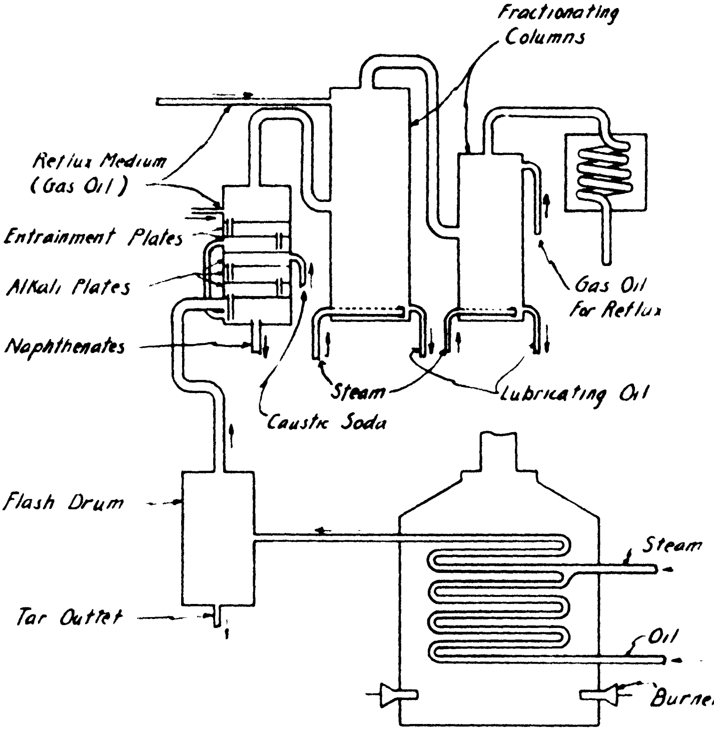

FIG. 269.—Equipment Assembly for Removal of Naphthenic Acids from Hydrocarbon Oils. (F. M. Rogers)

which may be drawn off at intervals. In place of the aqueous alkaline solution a suspension of soda-lime in a mixture of naphthenic soaps and oils has been proposed.[10] This extraction medium may be regenerated by the addition of caustic soda. Another procedure comprises conducting the oil vapors through a body of molten, substantially anhydrous alkali.[20] Thus, a mixture of steam and oil is heated to 750°F. in a pipe still (Fig. 269) and conducted to a flash drum, where the tarry constituents are removed. The vapor portion containing the naphthenic acids is then led to a bubble tower containing alkali plates and entrainment plates. Caustic soda is introduced at the top of the alkali plates to remove naphthenic acids and at the same time gas oil is admitted at the upper end of the bubble tower to maintain reflux. Campbell[21] suggests elimination of acidic constituents by scrubbing straight-run distillates with 15 per cent sodium carbonate solution. Phenols may be taken out subsequently by employing 10-20 per cent sodium hydroxide solution.

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[18] R. C. Wheeler and P. W. Prutzman, U. S. Reissue 19,179, May 22, 1934, to General Petroleum Corp. of Calif.; *J. Inst. Pet. Tech.*, 1934, **20**, 463A; *Chem. Abs.*, 1934, **28**, 4586. See also, U. S. P. 1,784,262, Dec. 9, 1930; *Chem. Abs.*, 1931, **25**, 409; *Brit. Chem. Abs.* **B**, 1931, 795.

[19] J. B. Hibou, Dutch P. 36,230, 1935, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 2743.

[20] F. M. Rogers, U. S. P. 2,007,146, July 2, 1935, to Standard Oil Co. of Indiana; *Chem. Abs.*, 1935, **29**, 5645; *J. Inst. Pet. Tech.*, 1935, **21**, 383A; *Brit. Chem. Abs.* **B**, 1936, 730.

In another process, petroleum fractions containing naphthenic acids and phenols are extracted with liquid sulphur dioxide.[22] The extract is then admixed with sodium carbonate to form naphthenates and phenolates. Sulphuric acid is incorporated in an amount sufficient to acidify the mixture. The latter is neutralized with sodium carbonate. In this manner sodium naphthenate is said to be formed, while the phenols are unaffected. These substances may then be separated by fractional distillation.

Several methods have been described for working up the oily still bottoms obtained on the distillation of lubricating oils, or other petroleum fractions, from alkalies. In one of these, the bottoms are heated with water under pressure and the mixture then cooled under the same condition. In this manner boiling of the water is prevented and consequently the formation of emulsions. The hydrocarbon and aqueous soap layers are withdrawn separately.[23] Recovery of the acids may be accomplished by acidifying the soap solution with a mineral acid, adding xylene and distilling to remove water, and extracting the residue with ethyl alcohol.[24] In other instances the water-free alkaline still bottoms are treated with concentrated sulphuric acid to liberate naphthenic acids and these extracted with a solvent.[25] Dilute acid (3-5 per cent) has been recommended instead of concentrated for the decomposition of alkaline bottoms and after separation of the solution of naphthenic acids in oil (adding gas oil if necessary to effect demulsification) the latter may be subjected to cracking to furnish a motor fuel.[26] This process is illustrated diagrammatically in Fig. 270. It has been pointed out that alkaline sludge may be treated with calcium hydroxide and gas oil to effect the removal of naphthenic acids.[27] The latter are converted to copper naphthenates which are said to dissolve in the gas oil. In this manner two layers are said to be formed; the lower an aqueous solution of sodium hydroxide, the upper the naphthenic soaps in gas oil. The soaps may then be converted into free acids by incorporating sulphuric acid in the upper layer. Also, it has been recommended that alkaline sludge be emulsified with water in the presence of a light oil which serves as a diluent.[28] The emulsion is then acidified with sulphuric acid to free the naphthenic acids, which separate together with the diluent oil. The latter mixture is removed, the diluent separated, and the naphthenic acids subjected to vacuum distillation. A flow diagram of this process is indicated in Fig. 271.

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[21] S. E. Campbell, *Refiner*, 1935, **14**, 381; *Chem. Abs.*, 1935, **29**, 8302

[22] R. Wischin, *3me Congres International du Petrol (Bucharest)*, 1907, **2**, 622; *Petroleum*, 1908, **3**, 1062; *Chem. Abs.*, 1909, **3**, 708; *J.S.C.I.*, 1908, **27**, 850; *Oesterr. Chem. Tech. Ztg.*, 1908, **27**, 20; *Chem. Abs.*, 1909, **3**, 1078. D. R. Merrill and A. L. Blount, U. S. P. 2,000,244, May 7, 1935, to Union Oil Co. of Calif.; *Brit. Chem. Abs.* **B**, 1936, 486; *Chem. Abs.*, 1935, **29**, 4167. See also, G. B. Gurvich, *Azer. Neft. Khoz.*, **1935**, No. 5, 103; *Chem. Abs.*, 1936, **30**, 3987.

[23] H. F. Angstadt, U. S. P. 1,931,880, Oct. 24, 1933, to Sun Oil Co.; *Brit. Chem. Abs.* **B**, 1934, 791; *Chem. Abs.*, 1934, **28**, 633.

[24] G. Alleman, U. S. P. 1,931,855, Oct. 24, 1933, to Sun Oil Co.; *Brit. Chem. Abs.* **B**, 1934, 615; *Chem. Abs.*, 1934, **28**, 669.

[25] R. Brunck, A. Kreutzer and W. Boeck, U. S. P. 1,938,513, Dec. 5, 1933, to Deutsche Gasolin. A.-G.; *Chem. Abs.*, 1934, **28**, 1182; *J. Inst. Pet. Tech.*, 1934, **20**, 115A.

[26] G. Kaufman and C. E. Lauer, U. S. P. 1,986,775, Jan. 1, 1935, to Texas Co.; *Brit. Chem. Abs.* **B**, 1935, 1127; *J. Inst. Pet. Tech.*, 1935, **21**, 137A; *Chem. Abs.*, 1935, **29**, 1231.

[27] Ya. S. Susanov, *Neft*, 1935, **6** (4), 19; *J. Inst. Pet. Tech.*, 1936, **22**, 347A; *Chem. Abs.*, 1936, **30**, 3987.

[28] R. F. Nelson and L. Zapf, U. S. P. 2,039,106, April 28, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 4312. *Cf.* W. B. Hendrey, Canadian P. 357,660, 1936, to Texaco Development Corp.; *Chem. Abs.*, 1936, **30**, 4312.

Wunsch[29] prepared naphthenates in the following manner. Alkali sludge was dispersed in water and then thinned with an organic solvent such as benzene, amyl alcohol or carbon tetrachloride. Demulsification of the mixture was effected by heating to 90-100°C. and adding an electrolyte, e.g., sodium chloride, after which the mineral oil layer was removed. Although alkali sludge may be dissolved in water and entrained hydrocarbons extracted therefrom with a solvent oil, nevertheless separation is not complete and some alkali naphthenates remain suspended in the solvent oil. A countercurrent system involving extraction of the oil suspension with water to remove alkali naphthenates and extraction of the aqueous solution with solvent oil to eliminate hydrocarbons is described by Hendrey.[30]

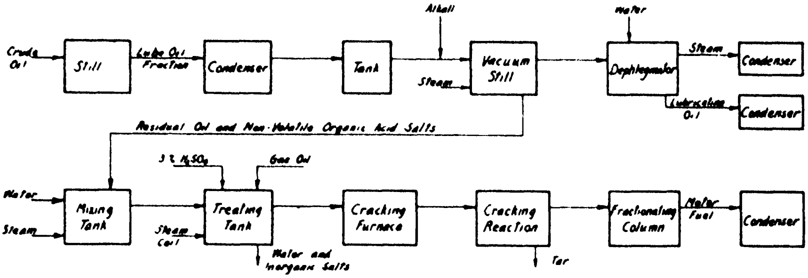

FIG. 270.—Flow Chart for Manufacture of Motor Fuel and Acid-free Lubricating Oil from Heavy Hydrocarbon Stock Containing Naphthenic Acids. (G. Kaufman and C. E. Lauer)

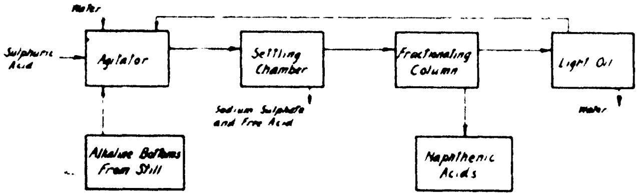

FIG. 271.—Flow Scheme for Recovery and Refining of Naphthenic Acids from Petroleum Oils. (R. F. Nelson and L. Zapf)

Also it has been reported that alkaline sludge may be combined with hydrogen fluoride to effect the separation of naphthenic acids.[31] The sludge is incorporated with calcium fluoride and sulphuric acid. The latter substances produce hydrogen fluoride

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

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[29] J. A. Wunsch, U. S. P. 2,003,640, June 4, 1935; *Chem. Abs.*, 1935, **29**, 4932; *Brit. Chem. Abs.* B, 1936, 585. The use of sodium chloride in recovering naphthenic acids is discussed by E. Schmitz, *Compte-rendu du congrès du graissage Strasbourg*, 1931; *Chem. Zentr.*, 1932, **2**, 2768. Roumanian P. 5 067, 1920.

[30] W. B. Hendrey, Canadian P. 349,973, 1935, to Texaco Development Corp.; *Chem. Abs.*, 1935, **29**, 4933.

[31] E. Schmitz, *Chimie et industrie*, 1925, Sept. Special No., 198; *Chem. Abs.*, 1926, **20**, 2743. German P. 370,606, 1921; *J.S.C.I.*, 1923, **42**, 643A; *Chem. Zentr.*, 1923, **2**, 1046.

which then interacts with the sodium naphthenates to free the naphthenic acids,

$$RCOONa + HF \longrightarrow RCOOH + NaF$$

where *R* represents a cycloparaffin with an alkyl side chain. Sodium fluoride may be transformed into calcium fluoride by calcium hydroxide. In this manner a recovery of 90 per cent of the caustic soda and 99 per cent of the naphthenic acids is said to be secured.

PURIFICATION OF CRUDE NAPHTHENIC ACIDS

The crude acids recovered by acidifying alkali sludge from refining of mineral oils are for the most part dark-colored, disagreeable smelling liquids boiling between 120°C. (at 12 mm.) and 300°C. (at 0.1 mm.).[32] The impurities are primarily hydrocarbons and some phenolic bodies. Methods which have been proposed for the purification of these acids include fractional distillation, reaction with basic compounds, such as aniline, followed by separation of the salt formed, and extraction of naphthenic soaps (either in the dry state or dissolved in a solvent.)[33] Goldberg and Shaverdova,[34] however, report that acids of high molecular weights easily decompose when subjected to distillation.

Deodorization may be accomplished by treating crude acids with oxidizing or reducing agents, or by heating their soap solutions to high temperatures under pressure. Bagirov[35] suggested heating a mixture of alkali sludge (soaps) and kerosene with steam and simultaneously agitating with air. Afterwards the mixture is allowed to settle and the lower layer, consisting of soap and kerosene, is withdrawn. The kerosene can be separated by distillation. Rabinovich and Osenova[36] described a method in which bleaching and deodorization of naphthenic acids is effected. The latter are dissolved in gasoline (50 per cent solution) and treated with small proportions of concentrated sulphuric acid. After removal of acid sludge, the gasoline solution is further treated at 50-60°C. with 5-10 per cent of an adsorption agent (gumbrin[36a]), filtered, and washed with an aqueous solution of an electrolyte, such as zinc or calcium chloride. This procedure is said to yield a product which is more homogeneous and stable than the crude acids but possessing somewhat less acidity. The foaming power of the corresponding potassium soaps is also slightly lower than that from unpurified acids.

It has been stated that the removal of color and odor from naphthenic acids may be accomplished by distilling a mixture of crude naphthenic acids to remove any carbonaceous materials.[37] The naphthenic acids are then redistilled in the presence of copper oxide. In another procedure the crude acids are admixed with air and nitrogen dioxide at 245-300°C.[38] The oxidizing agents are employed in an amount 50 times as great as the volume of the liquid naphthenic acids. Also, the acids may be filtered through an adsorbent such as fuller's earth.[39]

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[32] J. v. Braun, *Chem.-Ztg.*, 1935, **59** (48), 485; *Chem. Abs.*, 1935, **29**, 5429; *Brit. Chem. Abs.* **B**, 1935, 618; *J. Inst. Pet. Tech.*, 1935, **21**, 298A.

[33] For a description of the various methods of purification, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, **1934**.

[34] D. Goldberg and E. Shaverdova, *Azer. Neft. Khoz.*, **1933**, No. 11-12, 122; *Chem. Abs.*, 1934, **28**, 7491.

[35] K. Bagirov, *Neft*, 1931, **2** (15), 19; *J. Inst. Pet. Tech.*, 1936, **22**, 108A; *Chem. Abs.*, 1936, **30**, 3975.

[36] A. Rabinovich and T. Osenova, *Masloboino-Zhirovoe Delo*, 1934, **10** (12), 41; *Chem. Abs.*, 1935, **29**, 8304.

[36a] Gumbrin is an adsorbent earth similar in type to floridin. For a discussion of these and other adsorbents (and of permutites) see A. L. Lyubimov, *Trans. Inst. Econ. Mineral. (U.S.S.R.)*, **1933**, (10-year Vol.), 73; *Chem. Abs.*, 1935, **29**, 2314.

[37] F. J. Ewing, U. S. P. 2,035,696, March 31, 1936, to Union Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 3443.

[38] F. J. Ewing, U. S. P. 2,035,741, March 31, 1936, to Union Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 3443.

[39] F. J. Ewing, U. S. P. 2,035,742, March 31, 1936, to Union Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 3443.

Hendrey[39a] recommends treatment with concentrated sulphuric acid followed by distillation under reduced pressure. This type of operation is intended to provide a decolorization of the carboxylic acid.

CONSTITUTION AND CHEMICAL PROPERTIES OF NAPHTHENIC ACIDS

Although the term naphthenic acids has been employed broadly to designate acids found in crude petroleum or its distillates, nevertheless it appears that such acids containing up to 6 carbon atoms per molecule are aliphatic, those possessing 7 to 12 carbon atoms are monocyclic compounds, and those having more than 12 carbon atoms are dicyclic.[40] In some instances the low-molecular weight acids found in distillates are not present in the crude oil, thus indicating that such bodies are the result of pyrogenic decomposition. Furthermore, the main ring system, in the cyclic acids, is a cyclopentane ring and the carboxyl group is predominately on the end of an alkyl side chain attached to the single or a double ring structure.

FIG. 272.
Prof. Julius von Braun of Heidelberg, Germany. His researches have materially extended our knowledge of the chemical constitution of naphthenic acids.

One method of ascertaining whether the carboxyl group is connected to the cyclopentane nucleus through a CH_2 or CH group is that described by von Braun.[41] The naphthenic acid is converted (by ethylamine) to its ethylamide derivative and the latter is chlorinated with phosphorus pentachloride. This resulted in the formation of an imidechloride, $-CH_2C(Cl)=NC_2H_5$ or $>CHC(Cl)=NC_2H_5$, which in turn further reacted (with phosphorus pentachloride) to yield di- or monochlorinated derivatives, respectively,

$$-C(Cl)_2C(Cl)=NC_2H_5 \text{ or } >C(Cl)C(Cl)=NC_2H_5$$

Hydrolysis of the chlorinated imidechlorides gave the corresponding di- or monochloro naphthenic acid. In this manner an acid of the type RCH_2COOH furnished the product $RCCl_2COOH$, and $RCH(CH_3)COOH$ gave rise to $RCCl(CH_3)$-COOH.

[39a] W. B. Hendrey, U. S. P. 2,072,053, Feb. 23, 1937, to Texas Co.

[40] J. v. Braun, *Chem.-Ztg.*, 1935, **59**, 485; *J. Inst. Pet. Tech.*, 1935, **21**, 298A; *Chem. Abs.*, 1935, **29**, 2429; *Brit. Chem. Abs.* **B**, 1935, 618.

[41] J. v. Braun, F. Jostes and W. Munch, *Ann.*, 1927, **453**, 113; *Brit. Chem. Abs.* **A**, 1927, 547; *Chem. Abs.*, 1927, **21**, 2875. J. v. Braun, *Angew. Chem.*, 1934, **47**, 611; *Brit. Chem. Abs.* **A**, 1934, 1094; *Chem. Abs.*, 1934, **28**, 7252. See also, M. Naphtali, *Fettchem. Umschau*, 1933, **40**, 219; *Chem. Abs.*, 1934, **28**, 746; *Brit. Chem. Abs.* **B**, 1934, 312.

The number of chlorine atoms present in 100 molecules of the chlorinated acid was called the chlorine number. This value can be readily calculated by the formula

$$\frac{x}{100 - x} \cdot \frac{M}{35.5} \cdot 100$$

in which x is the percentage of chlorine in the product and M the molecular weight of the acid under investigation. Chlorine numbers of 200 and 100 denote acids consisting wholly of the types $—CH_2COOH$ and $>CHCOOH$, respectively, and intermediate numbers indicate a mixture. Thus, a value of 180 means that the sample contains 80 per cent of acids having the $—CH_2COOH$ group and 20 per cent of acids possessing the other group.

Two methods[42] are available for determining the number of carbon atoms in the chain attaching the carboxyl group to the cyclic nucleus: (1) the amine-olefin and (2) the progressive degradation. In the former, the naphthenic acid is reduced by hydrazoic acid to the corresponding amine, which in turn is converted to an olefin and the latter then oxidized. If an even number of carbon atoms were in the side chain the final product is an acid. An uneven number of carbon atoms gives rise to a ketone. In the second procedure, the acid is reduced to the alcohol from which the corresponding bromide, quarternary ammonium base, and olefin are prepared successively. The last-named derivative is subjected to oxidation. Again the final product is an acid or ketone indicating an even or odd number of carbon atoms, respectively, in the side chain.

The properties of naphthenic acids, in general, correspond to those of saturated aliphatic acids. The alkali salts are water-soluble and hydrolyze to about the same degree as the sodium or potassium soaps or fatty acids. The alkaline-earth and heavy-metal salts are insoluble in water, but soluble in organic solvents such as benzol or benzine. The acids may be converted into acid chlorides and these in turn into such derivatives as esters or amides. Esters of naphthenic acids, particularly those made from methyl alcohol, are well-known.[43] Reduction of the acids, their chlorides, or esters leads to the formation of naphthenic alcohols.[44] Also, it has been stated that naphthenic acids will interact with acetic anhydride to furnish the anhydrides of the naphthenic acids.[45]

APPLICATIONS OF NAPHTHENIC ACIDS

One use suggested for these acids is the breaking of various types of oil emulsions. For example, in the neutralization step following the acid treatment of certain lubricating oil distillates very stable emulsions are formed. The latter may be avoided, however, by the addition of naphthenic acids to the oil.[46] Demulsification of oil and water emulsions may be accomplished by employing a small proportion of a solution containing either 0.25 per cent naphthenic acids and 0.25 per cent sodium chloride or 0.2 per cent acids and 0.2 per cent sodium hydroxide.[47] Incorporation of the acids, or their salts, with low-grade mineral oils is said to increase the viscosity of such oils at ordinary temperatures but not at higher temperatures, e.g., 110-150°C.[48] Improvement in the color stability of gasolines is secured by the introduction of 0.001-0.5 per cent of naphthenic acids and 0.001-0.1 per cent of a red dye of the Sudan type.[49]

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[42] For a fuller description of these methods see, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

[43] For a comparison of the rates of esterification of paraffinic and cycloparaffinic acids with ethyl alcohol, see G. D. Advani and J. J. Sudborough, *J. Indian Inst. Sci.*, 1923, **6** (3), 41; *Chem. Abs.*, 1923, **17**, 3016; *J.C.S.*, 1923, **123** (1), 1009.

[44] For the reduction of tetramethylene carboxylic chloride with sodium and moist ether, see W. H. Perkin, Jr., *J.C.S.*, 1901, **79**, 329; *Chem. Zentr.*, 1901, 1, 776. The reduction of ethyl tetramethylene carboxylate is described by N. Ya. Demyanov, *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 837; *Chem. Abs.*, 1911, **5**, 3832; *J.C.S.*, 1910, **98** (1), 838. Other methods for preparing naphthenic alcohols from the corresponding acids are given by Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

[45] D. Holde, *Chem. Umschau*, 1923, **30**, 198; *Chem. Abs.*, 1923, **17**, 3615; *J.S.C.I.*, 1923, **42**, 896A.

[46] Z. Nekrasov, *Neft*, 1933, **4** (3 4), 18; *Brit. Chem. Abs.* **B**, 1935, 1032; *Chem. Abs.*, 1935, **29**, 2722.

According to Petrov,[50] artificial asphalts are obtained by heating petroleum acids to temperatures above 180°C. Swerissen[51] proposed adding an acid, e.g., acid sludge, to mineral oil residues containing naphthenic soaps and then subjecting the resulting mixture, containing the decomposition products of the soaps, to an oxidizing treatment to produce an asphalt.

Emulsifying, dispersing or softening agents are reported to be obtained by treating naphthenic acids with a mixture of sulphuric acid and its glycerol esters.[52] The reaction products of glycerol and naphthenic acids have been suggested as wetting and washing materials.[53] Loose, powdered compositions of the latter type can be prepared by incorporating water-soluble naphthenates of polyglycerol with alkali sulphates, such as sodium, ammonium or potassium sulphate.[54] Alkali meta- or pyrophosphates may be added. Naphthenic or sulphonaphthenic acids are said to increase the detersive power of soap solutions, the distilled acids from petroleum being a particularly effective ingredient in detergents.[55] Esters of naphthenic acids,[56] or of halogenated or alkyl substituted acids,[57] and partially etherized di- or polyhydric alcohols have been proposed as plasticizers for cellulose esters.

Insecticidal sprays can be prepared in the following manner.[58] A petroleum distillate (which may range from a light kerosene to a heavy lubricating oil) is emulsified with 5 per cent glyceryl naphthenate and water. A mixture of calcium caseinate (98 per cent) and aluminum sulphate (2 per cent) is dissolved in water and the solution incorporated with the emulsion to act as a spreader. The glyceryl naphthenate is reported to regulate the deposition of oil on plant leaves and to retard or prevent its absorption. Also, naphthenic acids have been suggested as solvents for insecticidal compositions, the latter being prepared from mercaptans and disulphides occurring in petroleum.[59]

According to Teichmann,[59a] esters resulting from the interaction of phenols and naphthenic acids may be dissolved in hydrocarbon oils or incorporated with oil-water emulsions to furnish insecticides and fungicides. On the other hand, Steik[59b] points out that the product obtained on heating the acids and castor oil at 270°C. for 1 to 1.5 hours is a neutral mutual solvent for castor oil and mineral oils.

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[47] N. Ryazanovskiĭ, *Neft*, 1933, 4 (17), 17; *Chem. Abs.*, 1935, **29**, 4563; *Brit. Chem. Abs.* B, 1936, 227. E. Schmitz, *Compte-rendu du congrès du graissage, Strasbourg*, 1931; *Chem. Zentr.*, 1932, **2**, 2768. B. M. Erlikh, *Neft*, 1934, 5 (7), 26; *Chem. Abs.*, 1936, **30**, 3987.

[48] Hungarian P. 112,747, 1935, to Vegyipari és Kereskedelmi Kft. (Successor to Ferenc Harsáyni); *Chem. Abs.*, 1935, **29**, 8316.

[49] E. G. Ulbricht, Canadian P. 354,707, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 2363.

[50] G. S. Petrov, Russian P. 31,130, 1933; *Chem. Abs.*, 1934, **28**, 3580.

[51] H. T. Swerissen, U. S. P. 2,026,073, Dec. 31, 1935, to Shell Development Co.; *Chem. Abs.*, 1936, **30**, 1226; *J. Inst. Pet. Tech.*, 1936, **22**, 107A.

[52] Swiss P. 175,870, 1935, to Chemische Fabrik vorm. Sandoz.; *Chem. Abs.*, 1936, **30**, 193. French P. 794,163, 1936; *Chem. Abs.*, 1936, **30**, 4591.

[53] French P. 767,788, 1934, to Farb- und Gerbstoffwerke Carl Flesch Jr.; *Chem. Abs.*, 1935, **29**, 532. See also, British P. 433,206, 1934; *Brit. Chem. Abs.* B, 1935, 940; *Chem. Abs.*, 1936, **30**, 539. G. A. Rubztov, *Neft*, 1935, 6 (6), 16; *Chem. Abs.*, 1936, **30**, 3980; *J. Inst. Pet. Tech.*, 1936, **22**, 364A. *Cf.* V. E. Parkhomenko, *Neft*, 1936, 7 (3), 25; *Chem. Abs.*, 1936, **30**, 6179.

[54] R. F. Furness and A. Fairbourne, British P. 439,435, 1935, to Lever Bros., Ltd.; *Brit. Chem. Abs.* B, 1936, 204; *Chem. Abs.*, 1936, **30**, 3134.

[55] A. Lomanovich and A. Filyukova, *Vsesoyuznuii NIRMMI*, **1933**, 78; *Chem. Abs.*, 1934, **28**, 5695.

[56] British P. 432,271, 1935, to British Celanese, Ltd.; *Brit. Chem. Abs.* B, 1935, 1137.

[57] G. Schneider, U. S. P. 2,016,392, Oct. 8, 1935, to Celanese Corp. of America; *Chem. Abs.*, 1935, **29**, 8000.

[58] H. Knight, Canadian P. 349,144, 1935, to Emulsoids Inc.; *Chem. Abs.*, 1935, **29**, 3766.

[59] T. P. Remy, U. S. P. 2,045,925, June 30, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 5716.

[59a] C. F. Teichmann, U. S. P. 2,015,045, Sept. 17, 1935, to Texas Co.; *Chem. Abs.*, 1935, **29**, 7572; *Brit. Chem. Abs.* B, 1936, 1118.

NAPHTHENIC ACID SOAPS AND THEIR USES

The alkali soaps of naphthenic acids compare favorably with those of fatty acids with respect to foam-producing and emulsifying qualities, degree of hydrolysis, and solubility in water. However, their application as detergent materials has been limited in many instances due to the disagreeable odor associated with them. It has been suggested that high-molecular weight acids be separated by distillation from those of low molecular weights as well as from resinous and asphaltic impurities, and that the soaps be subjected to a salting-out operation.[60] As previously mentioned, however, deodorization of naphthenic acids is often a very difficult task.[61]

Comparisons of the capacity of solutions of sodium soaps of rosin, ricinoleic, oleic and naphthenic acids for carrying suspended particles of manganese dioxide through filter paper were made by Tyutyunnikov and Kas'yanova.[62] This is analogous to the carbon number of soap solutions.[63] Of the soaps tested only sodium oleate effected passage of the dioxide particles through the paper. Measurements of the detergent (oil-removing) power of soap solutions (0.25-1.0 per cent concentration) indicated that naphthenic soaps were lacking in this property.[64] Nevertheless, the detergent action of ordinary (fatty acid) soap was decreased by incorporation of alkali naphthenates. On the other hand, addition of sodium carbonate to naphthenate soaps (alone or mixed with rosin soaps) increased their washing power. Other investigators, however, report that sodium naphthenates exhibit properties somewhat inferior to ordinary soaps but better than rosinates.[65] It has been noted that the presence of sodium carbonate diminished the amount of dye (Fast Yellow) adsorbed from an olein soap solution by carbon, did not affect the quantity removed from naphthenic acid soap, and increased the proportion adsorbed from rosin soap solution.[66] The detergent properties of naphthenic acids are utilized in washing textiles.[67] For example, a cellulose acetate fabric was wetted with naphthenic acids. At the end of a contact period of 2 hours the fabric was treated at 75°C. in a bath of aqueous caustic soda (containing 1 g. of sodium hydroxide per liter). In this manner a portion of the acid was said to be neutralized. The soap thus produced formed an emulsion with the free acid. Additional caustic soda was then incorporated to neutralize the bath and the fabric scoured at 75°C. in a bath containing 0.25 g. of sodium carbonate per liter of solution. The emulsion which formed was stated to contain any dirt in the fabric, so that the dirt was removed in the final scouring operation.

[59b] K. T. Steik, U. S. P. 2,068,088, Jan. 19, 1937, to National Oil Products Co.; *Chem. Abs.*, 1937, **31**, 1548.

[60] A. Duimshitz, *Masloboino Zhirovoe Delo*, 1935, 11, 260; *Chem. Abs.*, 1935, **29**, 8380. E. Schmitz, *Bull. soc. ind. Mulhouse*, 1913, **83**, 373; *J.S.C.I.*, 1913, **32**, 936.

[61] See for example, F. Ulzer, *Z. angew. Chem.*, 1900, **13**, 1273; *J.S.C.I.*, 1901, **20**, 112.

[62] B. Tyutyunnikov and N. Kas'yanova, *Allgem. Oel-u. Fett-Ztg.*, 1933, **30**, 11; *Chem. Abs.*, 1933, **27**, 4433; *Brit. Chem. Abs.* **B**, 1933, 274.

[63] The carbon number is defined as the number of grams of carbon black carried through the pores of a filter paper by 1 kilogram of soap solution: J. W. McBain, R. S. Harbone and A. M. King, *J.S.C.I.*, 1923, **42**, 373T; *Chem. Abs.*, 1923, 17, 3799.

[64] B. Tyutyunnikov, S. Pleshkova and A. Chernichkina, *Allgem. Oel-u. Fett-Ztg.*, 1933, **30**, 294; *Chem. Abs.*, 1934, **28**, 3259; *Brit. Chem. Abs.* **B**, 1933, 754.

[65] Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., New York, 1934.

[66] B. Tyutyunnikov and S. Pleshkova, *Allgem. Oel-u. Fett.-Ztg.*, 1934, **31**, 59; *Chem. Abs.*, 1934, **28**, 3608; *Brit. Chem. Abs.* **B**, 1934, 411.

[67] British P. 442,325, 1936, to British Celanese, Ltd.; *Brit. Chem. Abs.* **B**, 1936, 451; *Chem. Abs.*, 1936, **30**, 4690.

The emulsifying properties[67a] of naphthenic soaps together with their disinfectant[68] and insecticidal value render them useful as substitutes for fatty acid soaps in the preparation of petroleum emulsions for spraying compositions. Such emulsions are said to cause less damage to foliage than lime-sulphur.[69] An insecticide containing both naphthenates and sulphur is described by Berry.[70] Alkali wash liquors (from resin-forming light distillates) are acidified and the oily layer which separates is removed. Elemental sulphur is dissolved in it and then the naphthenic acids contained therein are neutralized with a base such as sodium carbonate.

Substantially anhydrous sodium naphthenate, made from acids having an average molecular weight of 225 and a distillation range of 230-310°C., may serve as a demulsification agent when mixed with a small proportion of free acids.[71] The influence of sodium hydroxide and sodium sulphate upon naphthenic soaps has been studied.[72] It was stated that aqueous solutions of naphthenic soaps, when treated with caustic soda and sodium sulphate, formed oil-in-water and water-in-oil emulsions. If the temperature is low, the formation of a water-in-oil emulsion was said to be favored. Heating of this emulsion causes it to break, the soap being transferred to the water. With oil-in-water emulsions, however, heating to 70-80°C. will not effect a separation, since an increase in the temperature causes the stabilization of this type of emulsion. If the oil-in-water emulsion is cooled without agitation the emulsion is reported to break, the soaps entering the oil phase. An oil-in-water emulsion reported to be applicable as a lubricant in cutting threads in pipes or bolts has been reported.[73] The oil is prepared by heating 15 per cent of sodium naphthenate to 180-300°F. (82-149°C.). A small proportion of rosin (5 per cent) and the same quantity of ethylene glycol is then incorporated.

Hendrey[73a] describes the preparation of a soluble oil by mixing 16 parts of sodium naphthenates, 1 to 5 parts of pine oil and about 2 per cent of water. Kaufman and Puryear[74] recommend a mixture of sodium stearate and sodium naphthenate dispersed in a heavy mineral lubricating oil. A small proportion of alkali (0.32 per cent) and a trace of water may be included.

Among the other uses for which naphthenic soaps have been suggested is the prevention of acid formation during the distillation of acid-treated mineral oil.[74a] A quantity of sodium naphthenate is added to the oil to take up any acid-reacting substance which may be evolved during the distillation. Also, it has been pointed out that naphthenic soap may be incorporated with ethylene glycol to form a fluid which may be employed in hydraulic brake systems.[75]

[67a] For the preparation of emulsions from distillates containing naphthenic acids, see H. T. Terrel. E. M. Hughes and P. L. Carter, U. S. P. 2,056,913, Oct. 6, 1936, to Sun Oil Co.; *Chem. Abs.*, 1936, **30**, 8600.

[68] Bacteriological tests made with neutral potassium naphthenates are described by D. J. Bachrach. *Soap*. 1934, 10 (11), 21; *Chem. Abs.*, 1935, **29**, 629; *Brit. Chem Abs.* **B**, 1935, 31.

[69] N. S. Vuisheleeskaya and M. M. Zarkin, *Bull. Plant Protection (U.S.S.R.)*, 1931, **3**, 215; *Chem. Abs.*, 1933, **27**, 5881; *J. Inst. Pet. Tech.*, 1934, **20**, 469A.

[70] A. G. V. Berry, U. S. P. 2,017,391, Oct. 15, 1935, to Trinidad Leaseholds, Ltd.; *Chem. Abs.*, 1935, **29**, 8220. See also British P. 428,542, 1935; *Chem. Abs.*, 1935, **29**, 6692; *Brit. Chem. Abs.* **B**, 1935, 743.

[71] M. DeGroote and A. F. Wirtel, U. S. P. 1,940,391, Dec. 19, 1933, to Tretolite Co.; *Chem. Abs.*, 1934, **28**, 1516. See also, G. Maksimovich, *Novosti Tekh Neftedobychi*, 1936, **4** (5), 6; *Chem. Abs.*, 1936, **30**, 6928; *J. Inst. Pet. Tech.*, 1936, **22**, 501A.

[72] R. M. Abramovich-Dvoretzkaya, *Azer. Neft. Khoz.*, **1935**, No. 2, 100; *Chem. Abs.*, 1935, **29**, 6409; *Brit. Chem. Abs.* **B**, 1936, 727.

[73] O. W. Neukom, U. S. P. 2,060.425. Nov. 10, 1936, to Union Oil Co. of Calif.

[73a] W. B. Hendrey, U. S. P. 2,058.788, Oct. 27, 1936, to Texas Co.; *Chem. Abs.*, 1937, **31**, 251.

[74] G. Kaufman and O. P. Puryear, U. S. P. 2,055,795, Sept. 29, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 8600.

[74a] B. Mead, U. S. P. 2,025,766, Dec. 31, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 1221; *Brit. Chem. Abs.* **B**, 1936, 821.

[75] M. R. Sherbino, U. S. P. 2,033,853, March 10, 1936, to Midland Steel Products Co.; *Chem. Abs.*, 1936, **30**, 3126.

Other Naphthenic Acid Salts

Of the heavy metal salts, the lead, cobalt and manganese naphthenates (Soligen driers) are probably the best known. They are widely employed as driers in paints and are reported to be more effective than the corresponding linoleates or resinates.[76] Knauss[77] considers that naphthenate driers differ from other types in that after precipitation of the anti-oxygens in the paint vehicle the remainder of the drier stays permanently in solution.

Although naphthenic acids are found in practically all petroleum oils nevertheless careful selection of the stock must be made to secure driers exhibiting the desired degree of solubility.[78] According to Kisselev and Norina,[79] these driers are prepared by adding a 10 per cent solution of the corresponding metallic salt to a 5 per cent solution of sodium naphthenate, the temperature being kept at 60° C. Acid naphthenates are said to be more soluble in oils than the basic or neutral salts both of which exhibit a pronounced tendency to precipitate from solutions in oils. Aqueous solutions containing a mixture of salts, e.g., lead nitrate and manganese chloride, may be employed and precipitation effected at the boiling temperature of the liquid.[80] Another procedure comprises reacting the metallic oxide with the acids in the presence of a liquid which is a solvent for the resulting naphthenate.[80a] Greenfield[81] points out that the acid fractions boiling between 280° and 300°C. are best for the production of lead and manganese salts, and those boiling at 270°C. yield the best cobalt salts. Meidert[82] suggested the addition of 6-10 per cent of a saturated fatty acid (e.g., palmitic acid) to naphthenate driers. Also, it has been pointed out that the salts of naphthenic acid will combine with halogenated olefins to furnish a drying oil.[83]

Copper naphthenate is proposed as a component of priming coats intended as preservatives for wood.[84] Cellulose esters, such as the trilaurate, together with ferric, lead, or copper naphthenate dissolved in an aromatic hydrocarbon as a solvent are reported to be anti-rust paints for iron.[85] Aluminum naphthenate admixed with glyceryl naphthenate or partially esterified glyceryl oleate is added to mineral oil distillates to furnish insecticidal sprays.[86] Electrical insulators may be obtained by immersing fibrous materials, e.g., tape or cords, in molten salts of naphthenic acids.[87]

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[76] M. D. Curwen, *Oil Colour Trade J.*, 1935, **88**, 1711; *Brit. Chem. Abs.* **B**, 1936, 160; *Chem. Abs.*, 1936, **30**, 1590. *Paint Manuf.*, 1936, **6**, 38; *J. Inst. Pet. Tech.*, 1936, **22**, 166A. H. W. Chatfield, *Paint Manuf.*, 1936, **6**, 70; *Chem. Abs.*, 1936, **30**, 3259.

[77] C. A. Knauss, *Off. Digest, Fed. Paint Varnish Prod. Clubs* No. **136**, 158; *Chem. Abs.*, 1934, **28**, 4612; *Brit. Chem. Abs.* **B**, 1934, 726.

[78] C. A. Klebstattel, *Off. Digest, Fed. Paint, Varnish Prod. Clubs* No. **135**, 112; *Chem. Abs.*, 1934, **28**, 3601; *Brit. Chem. Abs.* **B**, 1934, 510.

[79] V. S. Kisselev and L. I. Norina, *J. Khim. Prom.*, 1933, **10**, 22; *J. Inst. Pet. Tech.*, 1934, **20**, 259A. For a discussion of the application of naphthenic salts, see E. Schmitz, *Bull. soc. ind. Mulhouse*, 1913, **83**, 373; *J.S.C.I.*, 1913, **32**, 936.

[80] F. Pohl and B. Isenbeck, U. S. P. 1,974,507, Sept. 25, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 7561.

[80a] G. M. Fischer, U. S. P. 2,071,862, Feb. 23, 1937, to Socony Vacuum Oil Co.

[81] S. N. Greenfield, *Paint. Manuf.*, 1935, **5**, 154; *J. Inst. Pet. Tech.*, 1935, **21**, 275A; *Chem. Abs.*, 1935, **29**, 5679.

[82] F. Meidert, U. S. P. 1,976,182, Oct. 19, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 7561. See also U. S. P. 2,049,396, July 28, 1936; *Chem. Abs.*, 1936, **30**, 6586.

[83] A. Ya. Drinberg, Russian P. 39,293, 1934; *Chem. Abs.*, 1936, **30**, 3668.

[84] J. S. Remington, *Paint Manuf.*, 1936, **6**, 8; *Chem. Abs.*, 1936, **30**, 1594; *Brit. Chem. Abs.* **B**, 1936, 195. See also, H. C. Bryson, *Chem. Trade J.*, 1936, **98**, 445; *Chem. Abs.*, 1936, **30**, 5823; *J. Inst. Pet. Tech.*, 1936, **22**, 366A. *Oil Colour Trades J.*, 1936, **89**, 1912; *Chem. Abs.*, 1936, **30**, 5823.

[85] H. Schladebach and H. Hähle, U. S. P. 1,983,006, Dec. 6, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, **29**, 625.

[86] H. Knight, U. S. P. 1,949,799, Mar. 6, 1934, to Standard Oil Co. of Indiana; *Chem. Abs.*, 1934, **28**, 3171.

[87] P. A. Gulkovskii and M. E. Kellerman, Russian P. 32,588, 1933; *Chem. Abs.*, 1934, **28**, 3500.

Ammonium naphthenate is suggested as a coagulant for bituminous emulsions[88] and mixed with ammonium salts of petroleum sulphonic acids, which may be of the oil-soluble type,[89] as a demulsification agent for petroleum emulsions.[90] Butylated naphthalene sulphonic acid may replace the petroleum sulphonic acids.[91] In another method proposed for demulsifying petroleum emulsions, alkaline sludge containing free alkali is incorporated with the oil.[92] An undistilled heavy oil in the lubricating oil range and metallic salts of naphthenic acids are then added at 85-90°C.

Silicon carboxylates, derived from fatty or naphthenic acids, are said to be hydrogenation catalysts.[93] These may be prepared by reacting 1 mole of silicic-acetic anhydride with 4 moles of the carboxylic acid. Copper naphthenate is stated to be effective as a contact agent for the polymerization of butadiene.[94] When the diolefin was heated in the presence of the naphthenic salt, it was said that 45 per cent of the dimer was formed, but that no higher polymers were secured.

Metal salts of naphthenic acids have been used in the preparation of "extreme pressure" lubricants. Thus, a small proportion of aluminum naphthenate was incorporated in a mineral oil together with graphite.[95] The purpose of the naphthenic salt is to maintain the graphite, which is insoluble in oil, in a finely divided state. Also, the naphthenates are said to prevent formation of carbon on lubricated metal surfaces by peptizing the carbon and dispersing it in the oil. Another lubricant consists of a mixture of petroleum oil, sulphur and lead naphthenate.[96] The addition of tin naphthenate to oil intended for internal combustion engines is said to prevent oxidation and to increase the life of the oil.[97]

Metal salts of naphthenic acids, particularly copper naphthenate, have been employed as preservatives. In one instance, fishing nets were impregnated with a mixture of tar and copper naphthenate.[98] It was stated that with this mixture the nets retained 70 per cent of their initial strength after immersion in sea water for a period of 10 months. Also it has been reported that a copper naphthenate may be prepared in the fabric which is to be impregnated. A saturated aqueous solution of copper sulphate was poured into aqueous ammonium hydroxide (containing 25 per cent of the hydroxide) and naphthenic acids incorporated in the solution.[99] The product, which has a dark blue color, is then added to the fabric to be treated. It is stated that the ammonia evaporates, leaving a protective solid colloid which enables the fabric to withstand immersion in water for 6 months without losing its strength.

The corrosive action of crude oil containing sulphur compounds or salts of magnesium and calcium during distillation is said to be minimized to a large extent by the addition of zinc naphthenate to the crude oil.[100] The naphthenic salt was prepared by dissolving 1 volume of alkali sludge in 2 volumes of water at 90°C. and then incorporating zinc chloride in the solution. The resulting zinc naphthenate was removed from the mixture and dissolved in a gas oil heated to 95°C. The naphthenate solution was then incorporated in the crude oil before distillation of the latter.

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[88] H. Limburg, U. S. P. 1,984,023 and 1,984,024, Dec. 11, 1934, to Patent and Licensing Corp.; *Brit. Chem. Abs.* **B**, 1936, 53; *Chem. Abs.*, 1935, **29**, 905.

[89] M. DeGroote and A. F. Wirtel, U. S. P. 1,940,394, Dec. 19, 1933, to Tretolite Co.; *Chem. Abs.*, 1934, **28**, 1516.

[90] M. DeGroote, U. S. P. 1,940,396, Dec. 19, 1933, to Tretolite Co.; *Chem. Abs.*, 1934, **28**, 1516. See also U. S. P. 1,940,395, Dec. 19, 1933; *Chem. Abs.*, 1934, **28**, 1516.

[91] M. DeGroote and A. F. Wirtel, U. S. P. 1,940,392, Dec. 19, 1933, to Tretolite Co.; *Chem. Abs.*, 1934, **28**, 1516. See also U. S. P. 1,940,393, Dec. 19, 1933, to Tretolite Co.; *Chem. Abs.*, 1934, **28**, 1516.

[92] W. B. Hendrey and I. A. Ebaugh, U. S. P. 2,014,936, Sept. 17, 1935, to Texas Co.; *Chem. Abs.*, 1935. **29**, 7634; *Brit. Chem. Abs.* **B**, 1936, 681.

[93] A. Hintermaier, U. S. P. 2,017,000, Oct. 8, 1935, to Henkel & Cie. G.m.b.H.; *Chem. Abs.*, 1935, **29**, 8241. German P. 597,326, 1934; *Chem. Abs.*, 1934, **28**, 5080.

[94] A. I. Savel'ev, O. G. Arbidan and A. V. Zlatogurskii, *Sintet Kauchuk*, **1936**, No. 4, 18; *Chem. Abs.*, 1936, **30**, 7385. See also Chapter 26.

[95] French P. 797,625, 1936, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 7324.

[96] A. J. Morway, Canadian P. 358,686, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 5783.

[97] E. W. J. Mardles, *Petroleum Z.*, 1936, **32** (24); *Motorenbetrieb u Maschinen-Schmierung*, 1936, **9**, 6; *Brit. Chem. Abs.* **B**, 1936, 728.

[98] W. R. G. Atkins, *J. Marine Biol. Assoc. United Kingdom*, 1936, **20**, 627; *Brit. Chem. Abs.* **B**, 1936, 490; *Chem. Abs.*, 1936, **30**, 3653. W. R. G. Atkins and J. Purser, *J. Marine Biol. Assoc. United Kingdom*, 1936, **20**, 643; *Chem. Abs.*, 1936. **30**, 3917; *Brit. Chem. Abs.* **B**, 1936, 490.

[99] L. K. Adamyan, *Neft*, 1935, **6** (13), 16; *J. Inst. Pet. Tech.*, 1936, **22**, 367A.

Naphthenic salts of alkaline earth metals have been suggested as dispersion agents for carbon black to be employed in printing inks, lithographic varnishes or lacquers.[101] The carbon black is placed in an aqueous solution of sodium naphthenate and an alkaline earth salt added. In this manner the alkaline earth naphthenate which forms is said to be precipitated, carrying with it the carbon black in a finely dispersed state. The color, luster and gloss of the latter are said to be improved by the adsorption of magnesium, calcium, barium or strontium naphthenates.[101a] The naphthenates of such metals as zinc, lead, iron, titanium, nickel and copper are said to be efficient wetting agents in aiding the dispersion of pigments in printing ink vehicles.[102]

SULPHONATION OF NAPHTHENIC ACIDS

As a rule, naphthenic acids are soluble in concentrated sulphuric acid (with the evolution of heat) and are thereby sulphonated only to a limited extent. Gurwitsch[102a] states that treatment (of acids from kerosene) with 100 per cent of concentrated sulphuric acid for 1 hour at room temperature effected only 1.8 per cent sulphonation. The derivatives thus formed were readily separated from the unreacted bodies by washing with water. Pyhälä[103] reported that the acids from Russian kerosene distillates (which had not been refined with sulphuric acid) had a neutralization value of 230 and contained 0.1 per cent sulphur. When these were sulphonated the neutralization value rose to 240 and the sulphur content to 3.64 per cent. The disagreeable odor of the acids increased with sulphonation and this, Pyhälä considered, supported his contention that sulphur compounds were the cause of such odor.

According to Lidow,[104] sulphonation can be effected in the following manner: 100 parts of acids are agitated at room temperature for 2 days with 36.3 parts of sulphuric acid (66° Bé.). Afterwards the oily layer is washed with an aqueous solution of sodium sulphate or chloride, water alone furnishing a persistent emulsion. The product is then neutralized with sodium hydroxide solution (18° Bé.) and may be employed as a substitute for Turkey-red oil. Davidsohn,[105] however, failed to obtain sulphonated materials by this method and suggested another procedure. To 100 g. of acids are slowly added 300 g. of fuming sulphuric acid. After several hours the mixture is washed with an aqueous solution of sodium chloride. The resulting dark colored liquid, of disagreeable odor, had an SO_3 content of 7 per cent, and yielded fairly stable emulsions with water.

From the results of comparative dyeing tests Ulzer[106] concluded that sul-

[100] S. M. Silakov, *Neft*, 1934, **5** (17), 15; *Chem. Abs.*, 1936, **30**, 3979; *J. Inst. Pet. Tech.*, 1936, **22**, 208A.

[101] British P. 443,470, 1936, to Krebs Pigment and Color Corp.; *J. Inst. Pet. Tech.*, 1936, **22**, 222A; *Chem. Abs.*, 1936, **30**, 5376; *Brit. Chem. Abs.* B, 1936, 485. See also Chapter 8.

[101a] A. A. Brizzolara, E. L. Duhring and A. M. Erskine, U. S. P. 2,062,159, Nov. 24, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1937, **31**, 824.

[102] J. L. Burton, *Am. Ink Maker*, 1937, **15** (3), 22.

[102a] L. Gurwitsch and H. Moore, "The Scientific Principles of Petroleum Technology," D. Van Nostrand Co., Inc., New York, 1932.

[103] E. Pyhälä, *Petroleum*, 1914, **9**, 1506; *J.S.C.I.*, 1914, **33**, 781; *Chem. Abs.*, 1915, **9**, 372.

[104] J. P. Lidow, quoted by J. Davidsohn, *Z. angew. Chem.*, 1914, **27**, 2; *Chem. Abs.*, 1914, **8**, 1024.

[105] J. Davidsohn, *Seifensieder-Ztg.*, 1915, **42**, 285; *Chem. Abs.*, 1915, **9**, 1698.

[106] F. Ulzer, *Z. angew. Chem.*, 1900, **13**, 1273; *J.S.C.I.*, 1901, **20**, 112.

phonated naphthenic acids were not nearly as good as Turkey-red oil from castor oil, particularly as the former yielded a much less fiery red color. On the other hand it has been reported that in para red dyeing sulphonaphthenic acids were more effective in promoting dispersion of the color lake and reducing surface tension of the naphthol solution than castor-oil soap or soluble oil.[107]

Wetting, cleansing and emulsifying agents may be prepared by the action of sulphonating agents, e.g., chlorosulphonic acid, on mixtures of naphthenic acids and aromatic hydrocarbons or their amino, halogenated or hydroxy derivatives.[108] In place of the latter compounds, alcohols, mercaptans, ketones or carboxylic chlorides may be employed. Metallic salts of sulphonaphthenic acids are suggested as sizing materials for rayon yarns[109] and as addition agents for lubricating oils.[109a]

NAPHTHENIC ALCOHOLS

As previously mentioned, these alcohols may be obtained by catalytic reduction of the corresponding acids. A study of such compounds so prepared from (a) petroleum naphthenic acid and (b) from a spindle oil fraction was made by Lederer.[110] Although the alcohols in both instances were mixtures, nevertheless he concluded, from their boiling point curves,[111] that the product (boiling 165-274°C.) from the petroleum acids consisted principally of undeka- and dodeca-naphthenols, while those (boiling 335-375°C.) from the spindle oil were mainly eikosan- and heneikosan-naphthenols. The acetyl number and average molecular weight for the lower-boiling alcohols were 268 and 169, respectively, and these same values for the other material were 162 and 309, respectively. Lederer considered the constitutions of the alcohols were further substantiated by comparison of their physical properties (e.g., specific heat, viscosity, and interfacial tension against water) with those exhibited by 8-hexadecenecarboxylic acid, 9-octadecanol, octadecadiene, cyclohexanol, methyl cyclohexanol, and tetralin. The tendency of these two naphthenol fractions towards autoxidation was greater than that shown by oleyl alcohol or octadecene, but less than that for tetralin and cyclohexanol.

The rates of esterification of some polymethylene alcohols with acetic anhydride were investigated by Menschutkin.[112] His procedure was to dissolve equimolecular quantities of the alcohol and anhydride in benzene, and then heat the solution (in sealed tubes) for 24 hours at 100°C. At the end of this period, the proportion of acetic acid formed, according to the reaction

$$\mathrm{ROH} + (\mathrm{C_2H_3O_2})_2\mathrm{O} \longrightarrow \mathrm{ROOCCH_3} + \mathrm{CH_3COOH}$$

was determined by titration. The esterification constant (C) was calculated using the formula

$$C = \frac{x}{A - x} \cdot \frac{1}{t}$$

in which $A = 100$, x = per cent of ester formed, and t the time in minutes. His results for some pentamethylene alcohols are given in Table 206.

Menschutkin also noted that secondary alcohols from cyclic hydrocarbons were esterified more rapidly than secondary alcohols from aliphatics. This was illus-

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[107] P. P. Sazanoff, *Melliand Textilber.*, 1927, **8**, 275; *Chem. Abs.*, 1927, 21, 2068.

[108] German P. 623,108, 1935, to Oranienburger chem. Fab. A.-G.; *Chem. Abs.*, 1936, **30**, 2288.

[109] R. Böhme, German P. 577,831, 1933, to A. Th. Böhme Chem. Fabrik; *Chem. Abs.*, 1934, **28**, 658.

[109a] C. Tietig, U. S. P. 2,063,473, Dec. 8, 1936; *Chem. Abs.*, 1937, **31**, 854.

[110] E. L. Lederer, *Fettchem. Umschau*, 1935, **42**, 46, 75; *Chem. Abs.*, 1935, **29**, 7967.

[111] This method of boiling point analysis is described by E. L. Lederer, *Petroleum Z.*, 1935, **31** (6), 1; *Chem. Abs.*, 1935, **29**, 5637.

[112] N. Menschutkin, *J.C.S.*, 1906, **89**, 1532; *Chem. Zentr.*, 1906, **2**, 1724.

TABLE 206.—*Esterification Constants for Some Pentamethylene Alcohols.*

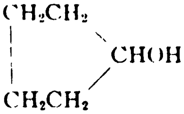
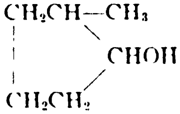
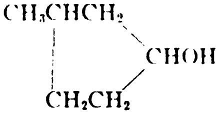
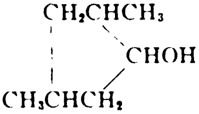
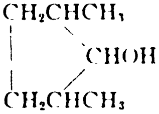
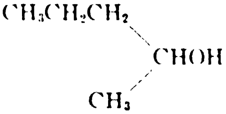
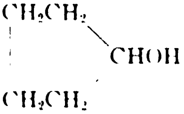
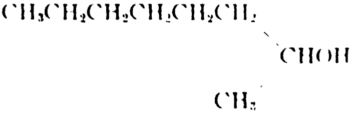
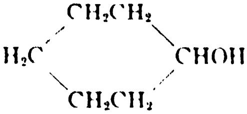
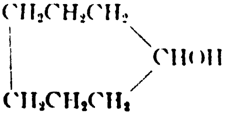
Alcohol	Boiling Point	Esterification Constant
	140.5°C.	0.0189
	148-149°C.	0.0126
	151-153°C.	0.0166
	154-155°C.	0.0131
	160-161°C.	0.0085

TABLE 207.—*Rates of Esterification of Aliphatic and Cyclic Secondary Alcohols.*

Alcohol	Esterification Constant
	0.0098
	0.0189
	0.0091
	0.0138
	0.0121

trated by comparison of the esterification constants for methyl propylcarbinol and cyclopentanol, and for methylhexylcarbinol and cyclohexanol or cycloheptanol (see Table 207).

Naphthenic alcohols have been suggested as solvents or emulsifiers in the preparation of pastes for carbon papers or ribbons.[113] Chlorination or sulphonation furnishes wetting or dispersing agents.[114] Esters of these alcohols and halogenated non-aromatic acids may be condensed with sodium derivatives of hydroxy compounds,[115] e.g., sodium phenolate, or with tertiary amines,[116] such as pyridine, to furnish products having saponaceous properties. Esters resulting from interaction of naphthenyl alcohols and polycarboxylic acids, anhydrides or chlorides are reported to be effective as plasticizing agents for cellulose esters and ethers.[117]

[113] French P. 757,735, 1933, to Deutsche Hydrierwerke A.-G.; *Chem. Abs.*, 1934, **28**, 3234.

[114] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

[115] A. Kirstahler and W. J. Kaiser, U. S. P. 2,010,727, Aug. 6, 1935, to Henkel & Co. G.m.b.H.; *Chem. Abs.*, 1935, **29**, 6607. Also British P. 408,749, 1934; *Chem. Abs.*, 1934, **28**, 5469; *Brit. Chem. Abs.* B, 1934, 534.

[116] British P. 408,754, 1934, to Henkel & Co. G.m.b.H.; *Chem. Abs.*, 1934, **28**, 5469; *Brit. Chem. Abs.* B, 1934, 534.

[117] H. J. Barrett and W. A. Lazier, U. S. P. 2,047,664, July 14, 1936, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 6007.

Chapter 49

Analysis of Natural Gas and Cracking Gas

Around the determination of the proportion of gases in mixtures there has grown up a considerable measure of technology. Exact determinations call for familiarity with the subject resulting from a sufficiently long experience on the part of the operator. Even so, reported gas analyses are frequently of a doubtful nature. For earlier work and data see "The Chemistry of Petroleum Derivatives," 1934 edition.

Natural gas, which is found to some extent in association with crude petroleum, consists essentially of a mixture of homologous hydrocarbons of the paraffin series. In the "dry" gases methane is the predominating constituent, while the "wet" gases[1] contain the higher homologues of methane in substantial amounts.[2] Besides gaseous and readily liquefiable hydrocarbons natural gases contain varying proportions of non-hydrocarbon gases, including nitrogen, carbon dioxide, hydrogen sulphide and helium. Carbon monoxide, hydrogen and unsaturated hydrocarbons are usually absent from natural gases.

Another important type of petroleum gas is that obtained as a by-product in the commercial cracking of higher petroleum fractions for the production of motor fuels and to which the name "cracking gas" or "cracked gas" has been applied. This differs from natural gas in its content of unsaturated hydrocarbons and hydrogen.[3] Quantities of carbon monoxide are also present, particularly when cracking is conducted in the presence of steam or oxygen.

The analysis of these complex mixtures of saturated and unsaturated hydrocarbons presents difficulties not encountered in the analysis of other gaseous fuels, such as coal gas or producer gas. In the latter, methane (associated with a small proportion of ethane) is the main saturated hydrocarbon constituent and ethylene the chief unsaturated component, so that absorption and combustion methods are adequate for a complete quantitative examination. In petroleum gases, however, at least three members of a homologous series occur together, and the precise analytical differentiation presents some difficulties, particularly in the paraffin series.

The ordinary methods of gas analysis may be used with appropriate modifications to analyze petroleum gases, but only in some cases can complete information be obtained. Most of the non-hydrocarbon constituents, including carbon dioxide, hydrogen sulphide, oxygen and carbon monoxide, may be estimated by absorptions in appropriate liquid reagents. Absorption in sulphuric acid of varied concentrations may be employed to show the total unsaturated hydrocarbon content. As the ordinary combustion and explosion procedures of analysis can be applied only to mixtures of two paraffin hydrocarbons, they are generally inadequate in the case of petroleum gases unless used in conjunction with some physical method of segregation. Two physical methods which have been developed involve the partial or complete separation of each component hydrocarbon by fractional condensation and fractional distillation. Analytical methods for the analysis of petroleum gases may thus be divided into absorption procedures, combustion or explosion processes, and physical methods of segregation. In general all three methods are necessary for the complete, quantitative examination of complex gas mixtures.

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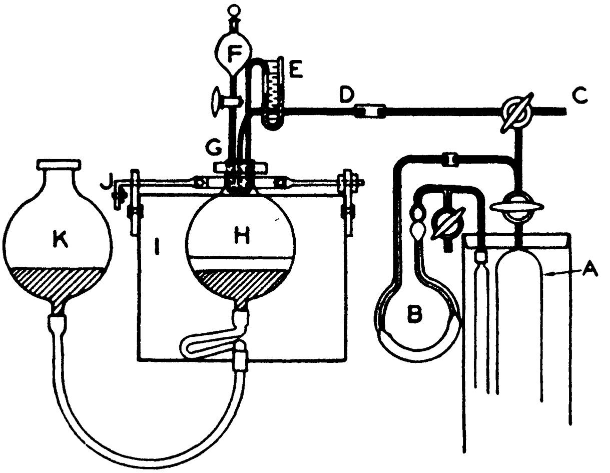
[1] Those gases containing appreciable quantities of easily liquefiable hydrocarbons.

[2] H. M. Stanley, *Proc. World Petroleum Congr., London*, 1933, **2**, 830; *J. Inst. Pet. Tech.*, 1934, **20**, 243A; *Brit. Chem. Abs.* **B**, 1934, 741; *Chem. Abs.*, 1934, **28**, 4871. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[3] For the composition of cracking gas, see Chapter 3.

ANALYSIS BY ABSORPTION

The analysis of natural gas and cracking gas by absorption depends upon the removal of an individual constituent, or a group of components, by treatment with appropriate liquid reagents in a definite order. By measuring the volume of gas remaining after each absorption, the composition of the mixture may be determined. However, the choice of liquids is difficult in some cases, particularly when unsaturated hydrocarbons are present. Some of the reagents employed in gas analysis, such as sulphuric acid, are capable of absorbing several constituents. When a definite order of absorption is employed this difficulty can be avoided to some extent.



A. Burette
B. Pressure compensator
C. Line for introduction of sample
D. Capillary line
E. Mercury manometer
F. Dropping funnel
G. Rubber stopper
H. Absorption bulb
I. Constant-temperature bath
J. Shaker
K. Leveling bulb

Courtesy Industrial and Engineering Chemistry

FIG. 273.—Apparatus for Study of Solubility of Carbon Dioxide in Salt Solutions. (K. A. Kobe and J. S. Williams)

The apparatus generally used consists of a gas burette or eudiometer enclosed in a water jacket (for temperature control) and containing a liquid levelling device (mercury, water or other liquid) for pressure control.[4] The gas is conducted from the burette into a pipette which holds the absorbent liquid. At the end of a definite period of time varying between 2 and 5 minutes, the gas is withdrawn and its volume remeasured. By successive absorption and measurement the volume of the other constituents, and the percentage composition, may be found. In some cases the change in pressure at constant volume is observed rather than the change in volume.

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[4] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. For a review of the progress of the natural and refinery gas industry, see G. A. Burrell, *Ind. Eng. Chem.*, 1934, 26, 143; *Chem. Abs.*, 1934, 28, 1840; *Brit. Chem. Abs.* B, 1934, 227.

In the description of the reagents for the absorption of the constituents of a gas mixture, the order of their use in analysis will be followed, at least in the case of the more common components, carbon dioxide, acetylene, other unsaturated hydrocarbons, and carbon monoxide.

Carbon dioxide is absorbed in a concentrated aqueous solution of potassium hydroxide prepared by dissolving 500 g. of stick potassium hydroxide in 500 cc. of distilled water.[5] According to Walter[6] sodium hydroxide may be employed instead of caustic potash. In this method the gases are conducted through a vertical tube in which they are mixed with a fine spray of caustic soda. The amount of carbon dioxide absorbed is determined by measuring the electrical conductance of the absorbent before and after passage of the gases.

The choice of a confining liquid[7] for gas analysis has received some attention. Kobe and Williams[8] made a study of the solubility of carbon dioxide in a number of aqueous solutions which have been recommended for this purpose. The apparatus consisted of a gas burette containing mercury. Carbon dioxide was collected in this burette and measured. An absorption bulb partly filled with mercury was connected to the burette. (See Fig. 273.) The solution which was being tested was then poured into the absorption bulb, after which the gases were forced into the bulb and the mixture agitated. At the end of 15 minutes the carbon dioxide was withdrawn and its volume remeasured. The results reported for a number of solutions may be seen in Table 208.

TABLE 208.—*Solubility of Carbon Dioxide, at 25°C. and Total Pressure 783.5 mm., in Salt Solutions.*

Salt Used	Concentration Weight %	Volume of Solution Ml.	Carbon Dioxide Dissolved Ml.	Carbon Dioxide Dissolved Ml./Ml.[a] Soln.
None		24.54	20.20	0.823
H_2SO_4	5	24.54	18.30	0.746
H_2SO_4	10	24.54	17.60	0.717
NaCl	10	24.54	13.52	0.551
NaCl	20	49.54	16.29	0.328
H_2SO_4	5			
NaCl	25	49.54	12.75	0.257
HCl	2			
Na_2SO_4	20	49.54	12.9	0.260
H_2SO_4	5 (vol.)			
Na_3PO_4	10	49.54	13.89	0.280
H_3PO_4	7			
$CaCl_2$	40	49.54	7.82	0.158
$MgCl_2$	30	49.54	8.12	0.164
$ZnCl_2$	50	49.54	19.12	0.386
$AlCl_3$	25	49.54	12.00	0.243
$Al_2(SO_4)_3$	20	49.54	10.96	0.221

[a] Milliliters of CO_2 at 25°C., 760 mm., dissolved per ml. of solution at 25°C.

The investigators point out that a concentrated solution of calcium chloride dissolves the least carbon dioxide but has a number of disadvantages which render it objectionable as a confining liquid. The solution is rather viscous, it is easily contaminated with impurities, in which case precipitates are formed, and when spilled it does not evaporate and leave crystals but remains as a sticky liquid. Magnesium chloride solution is much less viscous. However, the magnesium compound has been observed to form a precipitate of magnesium hydroxide when it comes in contact with the concentrated caustic potash and soda absorbents. Sodium sulphate is reported to be the most efficient of the compounds studied, since the addition of sulphuric acid to the sulphate does not increase the solubility of the carbon dioxide in the latter. This incorporation of acid is necessary, as a confining solution, it is stated, must not be alkaline.

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[5] E. A. Andreev and M. B. Neiman, *J. Applied Chem. (U.S.S.R.)*, 1935, **8**, 1100; *Chem. Abs.*, 1936, **30**, 5464.

[6] P. Walter, *Chimie et industrie*, 1934, *April Special No.*, 210; *Brit. Chem. Abs.* **A**, 1934, 743; *Chem. Abs.*, 1934, **28**, 5631.

[7] Liquid over which the gases are collected.

[8] K. A. Kobe and J. S. Williams, *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 37; *J. Inst. Pet. Tech.*, 1935, **21**, 126A; *Chem. Abs.*, 1935, **29**, 1355; *Brit. Chem. Abs.* **B**, 1935, 258.

Acetylene may be determined by absorption in an alkaline solution of potassium mercuric iodide prepared by dissolving 25 g. of mercuric iodide and 30 g. of potassium iodide in 100 cc. of water.[9] A small proportion of potassium hydroxide is added to the reagent just prior to use.

Among the methods suggested for the estimation of acetylene are absorption in ammoniacal cuprous chloride[10] or in a paste composed of cuprous chloride and aqueous caustic soda.[11] However, since these substances also absorb olefins, diolefins, and carbon monoxide to some extent, their application is limited.

Oxygen is estimated by absorption in an alkaline solution of pyrogallol[12] or by yellow phosphorus.[13] Brückner and Bloch[14] compared the activity of pyrogallol (1,2,3-trihydroxybenzene), sodium hyposulphite and 1,2,4-trihydroxybenzene. They report that the absorption rate and the total amount of oxygen absorbed in pyrogallol is greatest when potassium hydroxide is mixed with the phenol in the proportion of 1.5:1 by weight. However, if the gases under analysis contain more than 25 per cent of oxygen, the pyrogallol decomposes and carbon monoxide is produced. This difficulty is said to be eliminated by the use of 1,2,4-trihydroxybenzene (1,2,4-benzenetriol) and potassium hydroxide in the ratio 1:5.5 by weight. The rate of absorption in alkaline sodium hyposulphite, it is stated, is much slower than with either of the above reagents. One mole of the hyposulphite takes up only 0.94 moles of oxygen as compared with 1.5 moles for either of the trihydroxybenzenes, measured over the same period of time. According to Schmid[15] the amount of uncombined oxygen in a gas may be determined in the following manner. An alkaline solution of potassium iodide containing a small proportion of sodium potassium tartrate (Rochelle's Salt) is mixed with aqueous manganese chloride. The gases are then held in contact with this mixture for a period of 2 minutes to effect the absorption of oxygen. At the end of the contact time, the solution is acidified to liberate unreacted iodine, and the latter titrated with sodium thiosulphate.

Unsaturated hydrocarbons may be absorbed in a dilute solution of bromine in fuming sulphuric acid or in concentrated sulphuric acid containing 1 per cent of silver sulphate. Other procedures for the determination of the total quantity of unsaturated hydrocarbon gases involve use of an aqueous solution of bromine to minimize corrosion of mercury when the latter is employed as the confining liquid. Also fuming sulphuric acid is a rapid absorbent for all olefins but has the disadvantage that it slowly absorbs paraffin hydrocarbons.

Carbon monoxide may be estimated by conducting gases containing this substance through a vertical tube in which it is mixed with an atomized stream of aqueous ammoniacal cuprous chloride. The amount of carbon monoxide absorbed is determined by measuring the conductivity of the absorbing liquid before and after absorption.[16] Brückner and Gröbner[17] point out that a neutral solution of 125 g. of cuprous chloride and 265 g. of ammonium chloride in a liter of solution is best adapted for the determination of carbon monoxide. The rate of absorption of carbon monoxide in an acid solution of cuprous chloride is said to be increased by the addition of hydrochloric acid, but at the same time the total absorptive capacity decreases. According to these investigators, ammoniacal cuprous chloride shows a very low rate of absorption and absorbing capacity, irrespective of the amount of ammonium hydroxide present. Silver oxide has also been suggested as a reagent for the estimation of carbon monoxide.[18]

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[9] P. Lebeau and A. Damiens, *Compt. rend.*, 1913, **156**, 557; *Chem. Abs.*, 1913, 7, 1468; *J.C.S.*, 1913, **104** (2), 349.

[10] P. Walter, *Chimie et industrie*, 1934, *April Special No.*, 210; *Brit. Chem. Abs.* **A**, 1934, 743; *Chem. Abs.*, 1934, **28**, 5631.

[11] E. A. Andreev and M. B. Neiman, *J. Applied Chem. (U.S.S.R.)*, 1935, **8**, 1100; *Chem. Abs.*, 1936, **30**, 5464.

[12] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[13] E. A. Andreev and M. B. Neiman, *loc. cit.*

[14] H. Brückner and A. Bloch, *Gas- u. Wasserfach*, 1935, **78**, 645; *Chem. Abs.*, 1935, **29**, 7047; *Brit. Chem. Abs.* **B**, 1935, 947.

[15] A. Schmid, *Brennstoff-Chem.*, 1934, **15**, 271; *Brit. Chem. Abs.* **B**, 1934, 818; *Chem. Abs.*, 1934, **28**, 7073.

Hydrogen sulphide may be absorbed in pellets of manganese dioxide which have been soaked in phosphoric acid and from which all gas has been removed.[19] In one test with 90 cc. of illuminating gas 75 per cent of the hydrogen sulphide was absorbed by the reagent in 20 minutes, after which the remainder was taken up in a solution of copper sulphate acidified with sulphuric acid. Among the other reagents suggested are lead acetate[20] and iodine solutions.[21] When a gas sample is found to contain both hydrogen sulphide and sulphur dioxide, a comparison method is recommended.[22] Hydrogen sulphide and sulphur dioxide reduce iodine according to the equations:

$$\begin{aligned} H_2S + 2I &\longrightarrow 2HI + S \\ SO_2 + 2I + 2H_2O &\longrightarrow 2HI + H_2SO_4 \end{aligned}$$

The quantity of iodine reduced by conducting the gas under analysis directly through 0.1N iodine is compared with that reduced when the same volume of gas is passed through 40 per cent potassium hydroxide (to absorb hydrogen sulphide and sulphur dioxide) and then through 0.1N iodine in potassium iodide. In this manner other constituents which would also reduce iodine (e.g., olefins) can be quantitatively estimated. The difference in the number of cc. of iodine reduced in the two cases represents the volume of hydrogen sulphide and sulphur dioxide present. Roelen and Feisst[23] advocate the use of alkaline hydrogen peroxide for determining the sulphur compounds in gases. The gases are forced into a solution of 200 cc. of 0.5N sodium hydroxide and 100 cc. of 5 per cent hydrogen peroxide at the rate of 100 liters per hour.[24] A turbine stirrer rotating at 4000 r.p.m. is said to maintain an efficient contact between the gas and the liquid at this rate. The sulphur compounds are converted into sulphates and may be determined gravimetrically. One reported disadvantage of this method is the fact that any sulphur present in the form of thiophene is not absorbed.

Helium is usually determined as the residue after adsorption in charcoal of the gases in a specimen. In one form of apparatus a vertical gas burette is connected through the lower end to a mercury pump. At the upper end a glass tube leads to a bulb containing charcoal which is cooled with liquid air. (See Fig. 274.) From this bulb the gases flow to the lower end of the burette. In the tube between the burette and bulb there is a Plueckner tube[25] consisting of two platinum wires contained in a capillary tube through which a spark is passed. The procedure consists of forcing the gas to be tested into the burette after the latter has been evacuated. The volume of gas is measured and passed over the charcoal to adsorb all the constituents except helium. The latter is then introduced into the burette and its volume measured.[26] Anderson[27] suggests an analogous process in which natural gas is first conducted through a condenser tube which is surrounded by liquid air.

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[16] P. Walter, *Chimie et industrie*, 1934, *April Special No.*, 210; *Chem. Abs.*, 1934, **28**, 5631; *Brit. Chem. Abs.* **A**, 1934, 743.

[17] H. Bruckner and W. Gröbner, *Gas- u. Wasserfach*, 1935, **78**, 269; *Brit. Chem. Abs.* **B**, 1935, 590; *Chem. Abs*., 1935, **29**, 4550.

[18] E. A. Andreev and M. B. Neiman, *J. Applied Chem. (U.S.S.R.)*, 1935, **8**, 1100; *Chem. Abs.*, 1936, **30**, 5464; *Brit. Chem. Abs.* **B**, 1936, 50.

[19] A. Landgraf, *Chem. Fabrik*, 1935, **8**, 71; *Chem. Abs.*, 1935, **29**, 2693; *Brit. Chem. Abs.* **B**, 1935, 390.

[20] P. Walter, *Chimie et industrie*, 1934, *April Special No.*, 210; *Brit. Chem. Abs.* **A**, 1934, 743; *Chem. Abs.*, 1934, **28**, 5631.

[21] A. Schmid, *Brennstoff-Chem.*, 1934, **15**, 271; *Chem. Abs.*, 1934, **28**, 7073; *Brit. Chem. Abs.* **B**, 1934, 818.

[22] A. Gorn and E. Jakuba, *J. Applied Chem. (U.S.S.R.)*, 1934, **7**, 399; *Brit. Chem. Abs.* **B**, 1935, 6.

[23] O. Roelen and W. Feisst, *Brennstoff-Chem.*, 1934, **15**, 187; *Brit. Chem. Abs.* **B**, 1934, 660; *Chem. Abs.*, 1934, **28**, 6278.

[24] F. Heinrich and F. Petzold, *Z. anal. Chem.*, 1929, **76**, 120; *Chem. Abs.*, 1929, **25**, 1592; *Brit. Chem. Abs.* **B**, 1929, 231.

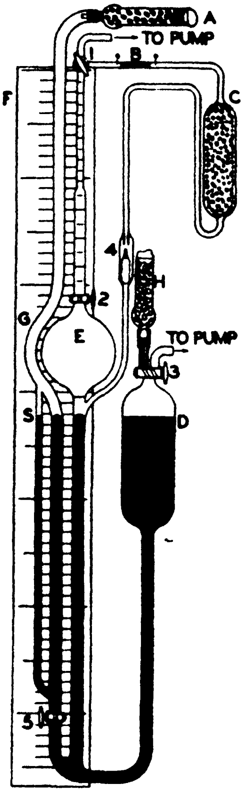

FIG. 274.
Diagram of Apparatus for Estimation of Helium in Gaseous Mixtures. (F. E. E. Germann, K. A. Gagos and C. A. Neilson)

A, H. Tubes containing calcium chloride
B. Pluecker tube
C. Tube containing charcoal
D. Mercury
E. McLeod gage
F. Calibrated scale
G. Mercury tube
S. Side tube

Courtesy Industrial and Engineering Chemistry

In this manner water vapor, carbon dioxide, ethane and heavier hydrocarbon gases are condensed. The remaining gas is then pumped through two connected tubes containing activated coconut charcoal. On issuing from the second of these tubes the gases are examined spectroscopically, and if helium alone is present the volume is measured.

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[25] A tube which may be used to detect the presence of gases spectroscopically.

[26] F. E. E. Germann, K. A. Gagos and C. A. Neilson, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, **215**; *J. Inst. Pet. Tech.*, 1934, **20**, **450A**; *Chem. Abs.*, 1934, **28**, 3623; *Brit. Chem. Abs.* **A**, 1934, **750**.

[27] C. C. Anderson, *Bur. Mines, Information Circ.*, 1934, No. **6796**; *Chem. Abs.*, 1934, **28**, 6982; *J. Inst. Pet. Tech.*, 1934, **20**, **525A**. *Cf.* **B. M. Nakashidze**, *Azer. Neft. Khoz.*, **1934**, No. 6, 30; *Chem. Abs.*, **1934**, **28**, 6980; *Brit. Chem. Abs.* **B**, 1935, 225.

Blacet and MacDonald[28] have described a method for the microanalysis of gases containing hydrogen, carbon monoxide, hydrogen chloride and ammonia. The samples were confined in a burette over mercury and the volume of the constituents estimated before and after inserting the proper absorbent. (See Fig. 275.) A bead made by fusing together cupric oxide and potassium hydroxide on a platinum loop was said to be satisfactory for absorbing hydrogen completely in 15 minutes. Carbon monoxide may be absorbed by the same reagent, hydrogen chloride by a solution of concentrated potassium hydroxide in a sintered glass bead, and ammonia by a moistened phosphorus pentoxide bead or by concentrated sulphuric acid in sintered glass.[29] A bath of molten lead was employed to maintain a constant temperature.

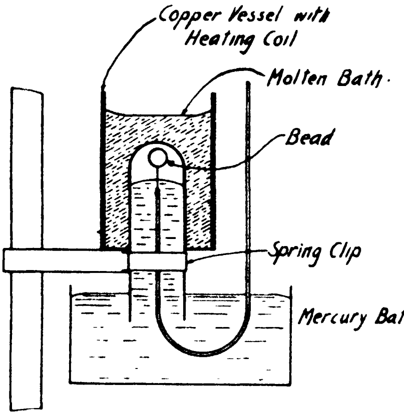

FIG. 275.
Sketch of Heater Employed in Microanalysis of Gases. (F. E. Blacet and G. D. MacDonald)

Courtesy Industrial and Engineering Chemistry

ANALYSIS BY COMBUSTION AND EXPLOSION

When the absorbable constituents of natural and cracking gases have been removed, paraffin hydrocarbons, hydrogen and nitrogen remain, together with some carbon monoxide and organic sulphur compounds. In the analysis of coal gas in which the paraffin is mainly methane, determination of this gas is a relatively easy matter. Hydrogen is oxidized to water by copper oxide at 280°C. or by palladium sponge at 100°C. and the residual methane-nitrogen mixture is then exploded with excess of air.[30] However, with natural or cracking gas in which a number of homologous gaseous paraffins are present the above method is not directly applicable. It therefore becomes necessary to effect some fractionation of the constituents. A number of procedures for effecting such fractionation on an analytical scale will be discussed below. When the gas contains sulphur and carbon monoxide, these must also be determined. The sulphur content is ascertained first, the percentage of carbon monoxide being estimated together with hydrogen.

Organic sulphur may be determined by oxidizing the sulphur compounds to sulphates. In this procedure, the gas is heated with an excess of air, converting the sulphur compounds to sulphur dioxide. The latter is then absorbed in a sodium carbonate solution and is oxidized to sulphate by air according to the equations.[31]

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[28] F. E. Blacet and G. D. MacDonald, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 334; *Brit. Chem. Abs.* **A**, 1934, 1188; *Chem. Abs.*, 1934, **28**, 6392. For a method of handling and weighing absorption tubes, see D. F. Haymann, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 342; *J. Inst. Pet. Tech.*, 1936, **22**, 495A; *Chem. Abs.*, 1936, **30**, 7489.

[29] Semifused glass particles.

[30] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

$$\begin{aligned} SO_2 + Na_2CO_3 &\longrightarrow Na_2SO_3 + CO_2 \\ 2Na_2SO_3 + O_2 &\longrightarrow 2Na_2SO_4 \end{aligned}$$

Afterwards the excess alkali is titrated with standard hydrochloric acid solution, employing methyl orange as an indicator. If the sodium carbonate solution is made up by dissolving 3.306 g. of the anhydrous salt in a liter of solution, 1 cc. of the solution will be equivalent to 0.001 g. of sulphur. Then if the acid solution contains 2.275 g. of hydrochloric acid per liter, 10 cc. of this solution will neutralize 10 cc. of the sodium carbonate solution. Using solutions of these strengths, the concentration of sulphur in the gas in grams per 100 cubic feet is given by the expression

$$\text{Sulphur concentration} = 1.543\,\frac{\text{cc. } Na_2CO_3 \text{ taken} - \text{cc. HCl used}}{\text{cu. ft. of gas burned}}$$

Carbon Monoxide. In addition to other well known methods, the gas may be determined by oxidation to carbon dioxide. According to Meyer and Slooff[32] iodine pentoxide will convert the monoxide to the dioxide at 120-130°C. Methane is said to be inert to the oxidizing agent at this temperature. To separate the iodine (liberated during oxidation) and methane the temperature is reduced to —80°C. at which iodine is condensed. The temperature is further reduced by liquid air to condense the carbon dioxide and part of the methane. Since methane has a considerable vapor pressure at this temperature (of liquid air) it may be removed by a mercury pump. The carbon dioxide may then be vaporized and measured in a gas burette. To obtain the sum of carbon monoxide and methane, a second sample is burned to carbon dioxide and measured as indicated above. Meyer and Slooff state that hydrogen reacts to some extent with the iodine pentoxide but does not influence the results within the limits of experimental error.

Hydrogen usually is estimated by oxidizing this gas to water and measuring the reduction in volume (or, in pressure at constant volume). A method developed for this purpose consists in passing the gas mixture very slowly over fresh copper oxide maintained at a temperature of 280°C. in a silica tube.[33] Treatment is continued until no further diminution in volume takes place, which usually requires about 30 minutes. This method is reported to be satisfactory when methane is the main gaseous paraffin constituent. Ethane and its higher homologues are said to be oxidized slowly in this manner, and, therefore, in the presence of large proportions of these substances, the method is unreliable. Among the other procedures suggested for the determination of hydrogen are oxidation in the presence of palladium in the form of a "sponge," wire, or colloidal solution.[34]

DETERMINATION OF THE PARAFFIN HYDROCARBONS BY OXIDATION

Methane may be determined by a slow combustion method employing cupric oxide.[34a] Walker and Christensen[35] state that a serious objection to this procedure is the danger of explosion. They suggest the use of a catalyst prepared by evaporation and subsequent thermal decomposition of 1.2 g. of cupric nitrate trihydrate and 14 g. of cobalt nitrate hexahydrate on 40 g. of unglazed porcelain particles. When the gas under analysis is passed over the catalyst mentioned above and subsequently over cupric oxide at a rate of 20-25 cc. per minute, the efficiency of the catalyst is reported to be at a maximum at a temperature of 500-550°C. as indicated in Fig. 276. The optimum ratio of oxygen to methane was said to be 3:1 by volume. In the procedure a single furnace with a compound combustion tube or two furnaces employing separate combustion tubes with a manifold may be used. Platinum has also been recommended as a catalyst for the oxidation of methane at temperatures in the range 800-900°C.[36] Kobe and Brookbank[37] report that platinized silica gel has no effect upon the oxidation of methane at 350°C., but that some carbon dioxide can be obtained at 370°C., though the reaction is not complete even at the latter temperature. The absorption of carbon dioxide by the catalyst is so small (1.35 cc. per gram at 0°C. and 740 mm. pressure) that it does not interfere with the results. A method for microanalysis of gases containing methane has been developed.[38] The apparatus consists of a length of glass tubing in which a platinum wire has been fused, so that the latter extends 1 cm. beyond the end of the glass tubing. This is placed in the gas holder and the reservoir below this holder filled with mercury. The gas containing the methane is then burned by heating the wire to a reddish orange glow.

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[31] C. W. Wilson, *Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 20; *Chem. Abs.*, 1933, **27**, 1137; ***Brit. Chem. Abs.*** **B**, 1933, 209.

[32] G. Meyer and A. Slooff, *Rec. trav. chim.*, 1935, 14, 800; *J. Inst. Pet. Tech.*, 1936, **22**, 91A; *Brit. Chem. Abs.* **A**, 1936, 42; *Chem. Abs.*, 1936, **30**, 699.

[33] J. G. King and L. J. Edgcombe, *Dept. Sci. Ind. Research, Fuel Research Tech. Paper*, 1931, No. **33**; *Chem. Abs.*, 1932, **26**, 4160; *Brit. Chem. Abs.* **B**, 1932, 215.

[34] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[34a] See, for example, P. K. Sakmin, *Khimstroi*, 1934, 6, 459; *Chem. Abs.*, 1935, **29**, 321; *Brit. Chem. Abs.* **B**, 1935, 341. V. A. Karzhavin, A. G. Leibush and E. A. Klevke, *Zavodskaya Lab.*, 1936, 5, 743; *Chem. Abs.*, 1936, **30**, 7495.

[35] I. F. Walker and B. E. Christensen, *Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 9; *Chem. Abs.*, 1935,

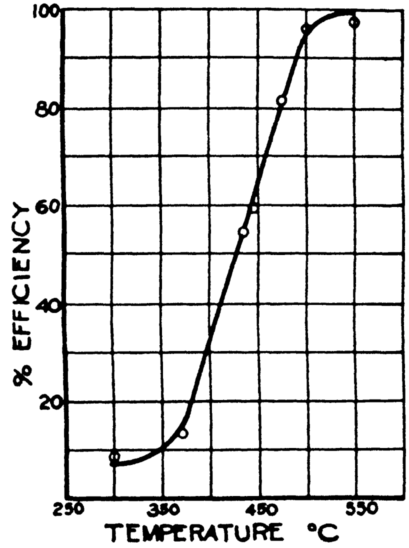

FIG. 276.
Influence of Temperature on Efficiency of Catalyst in Methane Determination. (I. F. Walker and B. E. Christensen)

Courtesy Industrial and Engineering Chemistry

Ethane is also said to be resistant to oxidation when platinized silica gel is present as a catalyst. At a temperature of 230°C. this hydrocarbon was not oxidized but at 270°C. some yields of carbon dioxide and water were secured. When the

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29, 1362; *Brit. Chem. Abs.* **B**, 1935, 261; *J. Inst. Pet. Tech.*, 1935, **21**, 125A. *Cf.* F. Schuster, G. Panning and H. Bülow, *Gas- u. Wasserfach*, 1935, **78**, 584; *Chem. Abs.*, 1935, **29**, 6732; *Brit. Chem. Abs.* **B**, 1935, 881.

[36] J. Herrmann, French P. 764,552, 1934; *Chem. Abs.*, 1934, **28**, 5782.

[37] K. A. Kobe and E. B. Brookbank, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 35; *Brit. Chem. Abs.* **A**, 1934, 269; *Chem. Abs.*, 1934, **28**, 991; *J. Inst. Pet. Tech.*, 1934, **20**, 167A.

[38] F. E. Blacet and D. H. Volman, *Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 44.

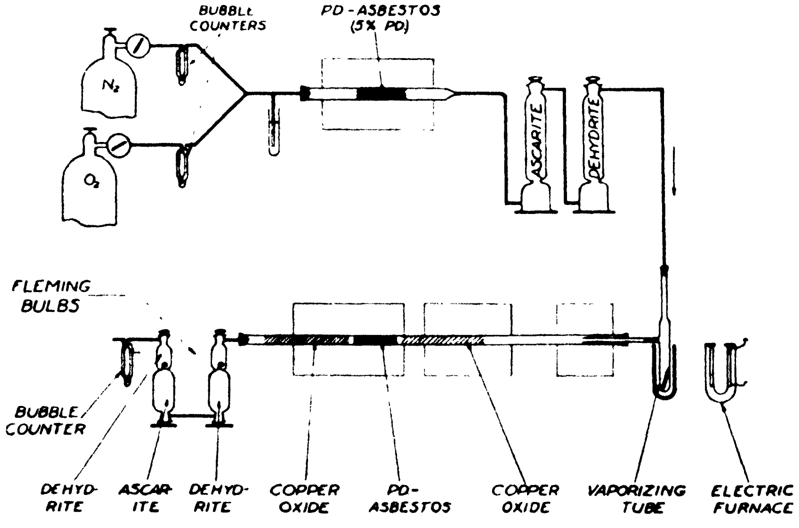
temperature reached 400°C. the reaction was still incomplete. Shepherd and Branham[39] conducted an investigation on the combustion of ethane to determine the amount of that hydrocarbon present in a sample of natural gas. The alkane was analyzed by a slow combustion method with excess oxygen and with a hot platinum spiral as contact agent. The contraction in volume of the gas upon burning, the volume of carbon dioxide produced and of oxygen consumed were measured. The volumes involved in the ideal gas reaction

$$\begin{array}{lcl} C_2H_6 + 3.5\ O_2 & \longrightarrow & 2CO_2 + 2.5 \text{ vol. contraction} \\ 1 \text{ vol.} + 3.5 \text{ vol.} & \longrightarrow & 2 \text{ vol.} + 2.5 \text{ vol. contraction} \end{array}$$

were said to be at variance with the observed volumes. An empirical equation which more nearly represents the results obtained was written as:

$$\begin{array}{lcl} C_2H_6 + 3.513\ O_2 & \longrightarrow & 1.994CO_2 + 2.52 \text{ vol. contraction} \\ 1 \text{ vol.} + 3.513 \text{ vol.} & \longrightarrow & 1.994 \text{ vol.} + 2.52 \text{ vol.} \end{array}$$

This would indicate that the contraction and oxygen consumed were higher than the ideal values and the carbon dioxide produced was lower. The sources of error which would influence the results include the solubility of carbon dioxide in the water in the apparatus and in the water formed in combustion, the solubility of the dioxide in the rubber parts of the apparatus, and losses of ethane by its solubility in the stopcock lubricant. To compare these results with those obtained from explosion methods, a series of analyses of pure ethane were made by explosion with: (1) commercial oxygen containing a small proportion (0.76 per cent) of nitrogen;



Courtesy Industrial and Engineering Chemistry

FIG. 277.—Combustion Apparatus for Highly Volatile Hydrocarbons. (J. H. Bruun and W. B. M. Faulconer)

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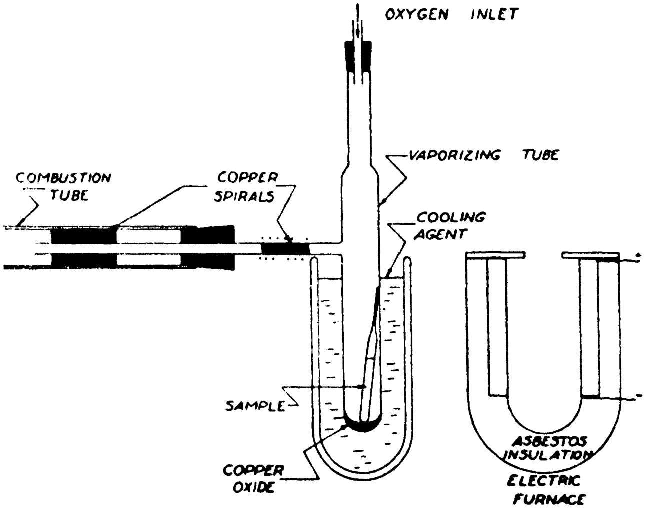
[39] M. Shepherd and J. R. Branham, *Bur. Standards J. Research*, 1933, 11, 783 (Research Paper No. 625); *J. Inst. Pet. Tech.*, 1934, 20, 240A; *Chem. Abs.*, 1934, 28, 991; *Brit. Chem. Abs.* A, 1934, 276.

(2) pure electrolytic oxygen and (3) air.[40] Relatively large differences were found between the various groups of analyses, with no group giving results which would correspond to the ideal equations. Some of the errors which might have caused these differences were examined. In the experiments in which commercial oxygen was used it was reported that oxides of nitrogen were formed in the explosion and influenced the values for the volumes of contraction and of oxygen consumed. In each of the three cases incomplete combustion was proved by finding carbon monoxide in the products of burning, amounting to 0.3 per cent of the sample. Slight additional contraction was also noticed when, after removing the carbon dioxide, the remaining gas was passed over the heated platinum spiral of the combustion pipette. This was said to be either unburned ethane from the original sample or ethane dissolved in the rubber and lubricant of the apparatus. The conclusion was reached that this procedure is not particularly efficient since results showing the presence of 5 to 15 per cent of methane were secured from a gas which was known to be pure ethane.



Courtesy Industrial and Engineering Chemistry

FIG. 277A.—Sketch of Vaporizing Tube Shown in Fig. 277.

Complete combustion of gas mixtures containing appreciable proportions of higher paraffins by passage over heated cupric oxide has been stated to be satisfactory. This method, although not quite quantitative, is said to furnish results of sufficient accuracy. Any carbon dioxide which is absorbed by the cupric oxide may be removed by treatment of the hot oxide with a stream of air. When the hydrocarbons have been completely oxidized to carbon dioxide and water, the resulting gas mixture may be removed from the cupric oxide by evacuation and the carbon dioxide and oxygen determined by absorption. To minimize the danger of explosions in the combustion method for analysis of propane, Bruun and Faulconer[41] have proposed controlled evaporation. The hydrocarbon is burned in a mixture of nitrogen and oxygen, as shown in Fig. 277. The samples to be analyzed are first cooled and enclosed in sealed Pyrex glass tubes drawn out into a fine capillary opening at one end. Each tube is then placed in a vaporizing tube (Fig. 277A) which has been cooled below the boiling point of propane (—42.2°C.). The tip of the sample tube is broken, and the rate of evaporation of the sample controlled by slowly lowering the cooling medium. If a residue remains in the tube after evaporation, it may be removed by heating the tube with an electric furnace.

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[40] J. R. Branham and M. Shepherd. *J. Research Natl. Bur. Standards*, 1934, **13**, 377 (Research Paper No. 715); *Chem. Abs.*, 1935, **29**, 427; *Brit. Chem. Abs.* **B**, 1934, 1093; *J. Inst. Pet. Tech.*, 1935, **21**, 90A.

[41] J. H. Bruun and W. B. M. Faulconer, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 315; *J. Inst. Pet. Tech.*, 1936, **22**, 497A; *Chem. Abs.*, 1936, **30**, 5467.

Koetschau and Schmitt[42] have described a combustion apparatus which is reported to be sensitive to gasoline concentrations of 0.1 per cent in air. It consists of a Wheatstone bridge with four wires which are in thermal equilibrium when surrounded by air. The mixture under analysis is burned by passage over one pair of wires which are electrically heated, while air is heated over the other pair in a similar manner. Changes in the resistance of the first pair of wires, due to the extra heat derived from the combustion, cause deflection of two galvanometer needles, one on a scale graduated to show the percentage (to as low as 1 per cent) of gasoline in the air, the other on a scale graduated in divisions which enable the detection of concentrations of 0.1 per cent.

ANALYSIS BY CONDENSATION

Absorption and combustion analyses are in themselves quite inadequate for a complete analysis of natural gases or of complex mixtures such as gases from cracking plants and hydrogenation units. A physical separation is necessary to completely determine the proportion of each of the alkanes, olefins and diolefins present. In general the mixed hydrocarbons are subjected to low-temperature condensation followed by fractional distillation.

The analytical separation of any individual hydrocarbon by fractionation from a mixture of homologous hydrocarbons becomes more difficult as the series ascends.[43] As the number of carbon atoms becomes greater, the vapor pressures of the individual hydrocarbons, hence their boiling points, tend to approach one another more closely. The difficulties associated with the fundamental analysis of hydrocarbon mixtures are thus quite obvious. Fortunately, there are only about 20 known gaseous hydrocarbons whose boiling points at atmospheric pressure are within a range of 170°C., and very few mixtures would probably contain them all.

Tropsch and Mattox[44] reported that a mixture of hydrocarbons condensed from a gas sample at the temperature of liquid nitrogen may be distilled into composite fractions containing 2 or 3 and 3 or 4 carbon atoms per molecule. The separation is effected without the use of a fractionating column by simple evaporation at controlled low temperatures (from —195° to —105°C.) and correspondingly low pressures (1 mm. of mercury) and by fractional condensation in a series of glass bulbs each cooled to the proper temperature by liquid nitrogen and by aluminum blocks containing this substance. In the procedure advantage is taken of the high vapor pressure ratios existing between the constituents at low temperatures. This difference of vapor pressure causes the rates of evaporation of each fraction to vary widely from that of every other fraction and makes possible the selection of temperatures such that the less volatile components possess in each case a negligible vapor pressure and the more volatile components relatively high vapor pressures. Since these condensation temperatures are fairly constant for the removal of each fraction, the separation may be accomplished by varying the pressure rather than the temperature. Another advantage reported to result from the use of low pressures is the fact that the actual amount of the vapor phase over the liquid phase is quite small at low pressures, so that a negligible percentage of the vapor phase remains above the liquid at the completion of each condensation, an important consideration where limited amounts of gas are at hand.

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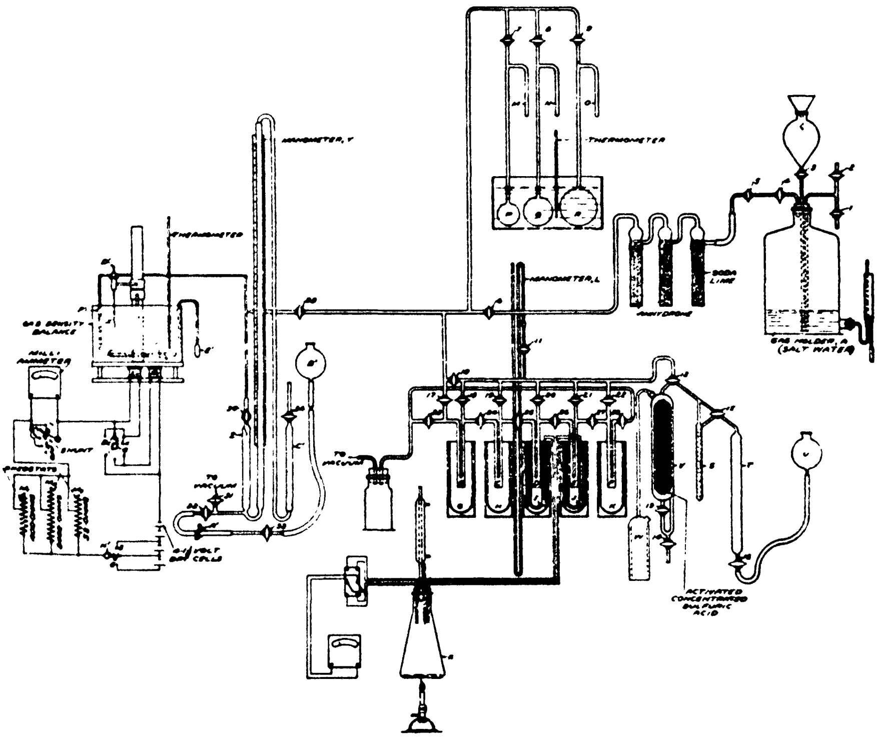
[42] R. Koetschau and G. Schmitt, *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 755; *J. Inst. Pet. Tech.*, 1935, **21**, 399A; *Chem. Abs.*, 1936, **30**, 3992. See also S. Mischonsniky, *Chim. & ind.*, 1934, April Special No., 258; *Brit. Chem. Abs.* A, 1934, 748; *Chem. Abs.*, 1934, **28**, 5631.

[43] Carleton Ellis, "The Chemistry of Petroleum Derivatives,' 'The Chemical Catalog Co., Inc., New York, 1934.

[44] H. Tropsch and W. J. Mattox, *Ind. Eng. Chem., Anal Ed.*, 1934, **6**, 235; *Chem. Abs.*, 1934, **28**, 5627; *Brit. Chem. Abs.* A, 1934, 1016. *Cf.* E. Berl and W. Forst, *Z. anal. Chem.*, 1934, **98**, 305; *Brit. Chem. Abs.* B, 1934, 996; *Chem. Abs.*, 1935, **29**, 80.



Courtesy Industrial and Engineering Chemistry

FIG. 278.—Apparatus Assembly for Analysis of Gaseous Hydrocarbon Mixtures. (H. Tropsch and W. J. Mattox)

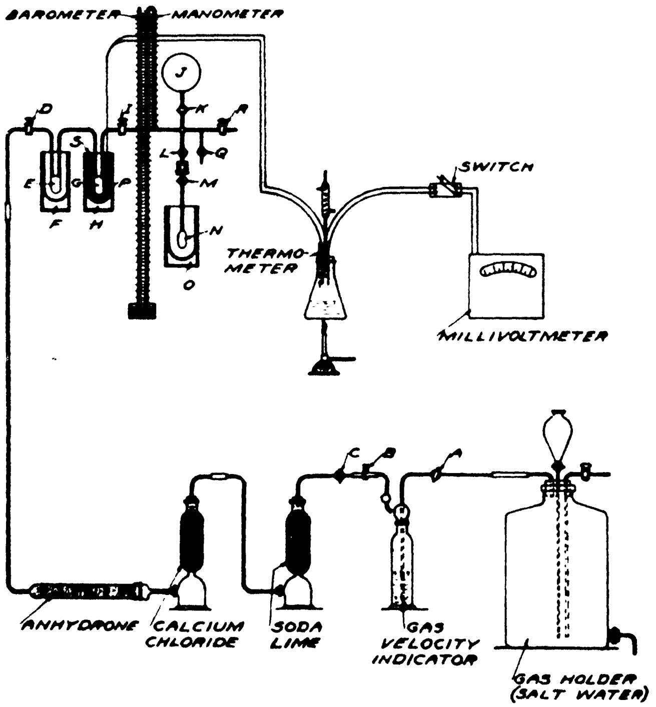
B, C, D, E, F. U-tubes
G, H, I, J, K. Aluminum blocks containing liquid nitrogen
M, N, O, S. Condensation tubes
P, Q, R. Calibrated volumetric bulbs
T. Burette
U. Leveling bottle
V. Pipette
Lc, Rc. Electromagnets
D'. Auxiliary magnet
F'. Glass joint
G'. Switch
H'. Switch
M_1, M_2, M_3. Resistances

Hydrogen, carbon monoxide, oxygen, nitrogen and methane are removed from the condensable hydrocarbons at the temperature of liquid nitrogen (—195°C.) by reducing the pressure to 0.1 mm., and the percentage of these constituents may be determined by absorption and combustion, as described previously. Acetylene is separated from the gas before condensation. The vapor pressure of ethane remains so low at the temperature of liquid nitrogen that none of it is removed with the methane distillate. Pentane and heavier hydrocarbons present in the gas mixture are quantitatively condensed from the butanes at a temperature of —105°C. and 1 mm. pressure. Fractionation of the remaining hydrocarbons into two composite fractions is made at 1 mm. pressure and at temperatures of —135 to —140°C. and at —195°C. The components of these fractions are listed in Table 209.

TABLE 209.—*Components of Hydrocarbon Mixtures Obtained by Fractional Condensation*

Fraction	Temperature of Condensation °C.	Constituents
1..............	−195	Ethane, ethylene, propane, propene
2..............	−135 to −140	Propane, propene, butane, butene
3..............	−105	Pentane and higher

Analysis of the first two fractions is made by density determinations, one on the mixture of paraffins and olefins and a second on the paraffins after the removal of



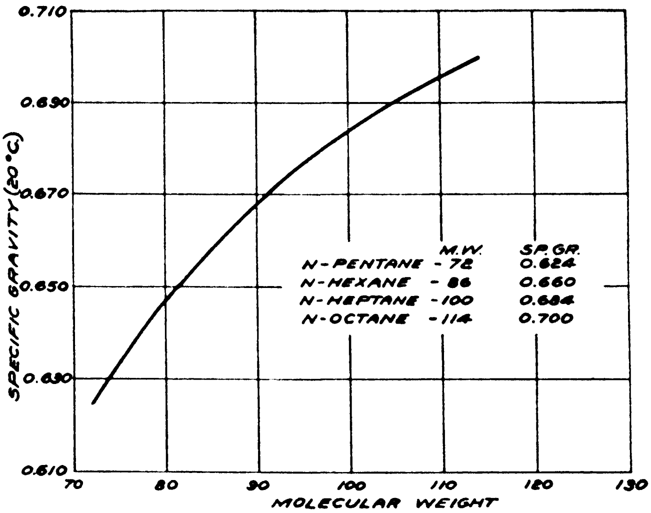
Courtesy Industrial and Engineering Chemistry

FIG. 279.—Apparatus for Determining Gasoline Content of Gases. (H. Tropsch and W. J. Mattox)

E. U-tubes
F. Dewar flask
G. U-tubes
H. Dewar flask
J. Volumetric bulb
N. Volumetric bulb
O. Dewar flask
P. Aluminum block
S. Hole for introduction of liquid nitrogen

the olefins by concentrated sulphuric acid activated by nickel and silver sulphates. The density of the olefins may be calculated from the change in the density of the fraction upon removal of these substances. The volume of each hydrocarbon and the per cent by volume of each hydrocarbon in the original sample may then be estimated from the known density of the two olefins, the known density of the two paraffins, and the volumes of olefins and paraffins.

The third fraction contains hydrocarbons which are liquids at temperatures below 20°C. This portion is reported as gasoline, either as grams per liter of gas, as volume per cent or as gallons of gasoline per 1000 cubic feet of gas, each of the calculations being made from the volume and density of the vaporized fraction. The density determinations of Tropsch and Mattox were made with a Stock electromagnetic gas-density balance which operates according to the principle of determining specific gravity by measuring the buoyancy produced on a small hollow quartz ball (fastened to a scale beam) by the influence of the surrounding gases. This is illustrated in Fig. 278. One of the reported advantages of this method is that relatively small samples, 500 cc. or slightly less, may be completely analyzed.



Courtesy Industrial and Engineering Chemistry

FIG. 280.—Relation of Specific Gravity to Molecular Weight for Hydrocarbons *n*-Pentane to *n*-Octane. (H. Tropsch and W. J. Mattox)

A somewhat similar procedure is suggested by the same investigators[45] for determination of the gasoline (i.e., easily liquefied vapors) content of gases. The sample is condensed at the temperature of liquid nitrogen and at atmospheric pressure. By reducing the pressure to 0.1 mm. of mercury, methane and other difficultly condensable gases (especially dissolved nitrogen) are removed. The condensate is then fractionated at −105°C., a temperature at which the hydrocarbons above C_4 are liquid. The hydrocarbons C_5 and higher are then vaporized into a known volume where the pressure and temperature can be measured. These gasoline vapors are condensed by liquid nitrogen in a bulb which may be removed from the apparatus and weighed. The apparatus is illustrated in Fig. 279. From the weight of the gasoline and the pressure it exerts when vaporized in a known volume at a definite temperature, the average molecular weight of the sample is calculated. By means of a curve relating the molecular weights to the specific gravities of the pure hydrocarbons (see Fig. 280) the specific gravity of the gasoline is read. With the weight of the gasoline from a known volume of gas and the specific gravity of the gasoline, the gallons of gasoline per 1000 cubic feet of gas at 60°F. (15°C.) and 30 inches (760 mm.) of mercury may be calculated from the formula:

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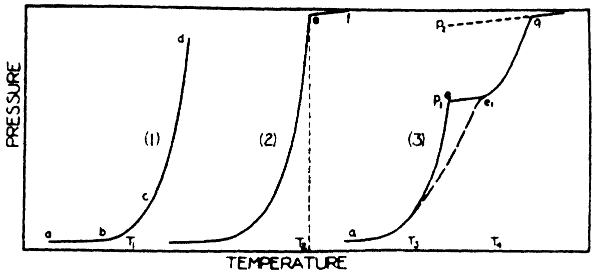
[45] H. Tropsch and W. J. Mattox, *Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 405; *Brit. Chem. Abs.* B, 1935, 54; *Chem. Abs.*, 1935, 29, 327.

$$G = \frac{19.39 \times g(t_1 + 273)}{S \times P \times V}$$

where G = gallons of gasoline per thousand cubic feet of wet gas at 60°F. (15°C.) and 30 inches (760 mm.) of mercury, g = weight of gasoline, grams, t_1 = temperature of gas sample, °C., S = specific gravity of gasoline at 20°C., P = pressure of gas sample, and V = volume (liters) of the gas sample.

Sebastian and Howard[46] suggest a method for the microanalysis of gaseous mixtures based upon the characteristic form of vapor pressure-temperature curves.



Courtesy Industrial and Engineering Chemistry

FIG. 281.—Idealized Pressure-Temperature Curves for Gases. (J. J. S. Sebastian and H. C. Howard)

If p, the pressure, is plotted against the absolute temperature, a curve of the form shown in Fig. 281, Curve 1, is obtained. From this curve it may be seen that for small values of pressure the latter increases only slightly even when there is a considerable change in the temperature. As the temperature increases over a longer range there is a rapid rise in the pressure, which is followed by a sharp, almost linear rise. The period of rapid change in pressure is designated by the investigators as the initial vaporization temperature. If a closed system of one component is studied, the relation of a vapor phase in equilibrium with its solid or liquid phase, is given by this curve. If, however, the system is sufficiently large so that the condensed phase ultimately disappears, the curve takes the shape indicated in Curve 2. If T_2 represents the absolute temperature at which the condensed phase disappears, the curve beyond this point represents the expansion of the vapor with rise in temperature the value of which is comparatively small.

If two substances form separate phases in the condensed states, and if the initial vaporization temperatures are sufficiently far apart, the more volatile compound will be relatively completely evaporated from the condensed phase before the vapor pressure of the second becomes appreciable. By plotting the pressure against the absolute temperature a curve of the form of Curve 3 (Fig. 281) will be obtained from which the quantitative composition may be determined. The initial vaporization temperatures T_3 and T_4 are characteristics of the components and represent the qualitative composition. The ratio of p_1 to p_2 gives the fraction by volume of the more volatile component present in the mixture, from which the quantitative composition may be calculated.

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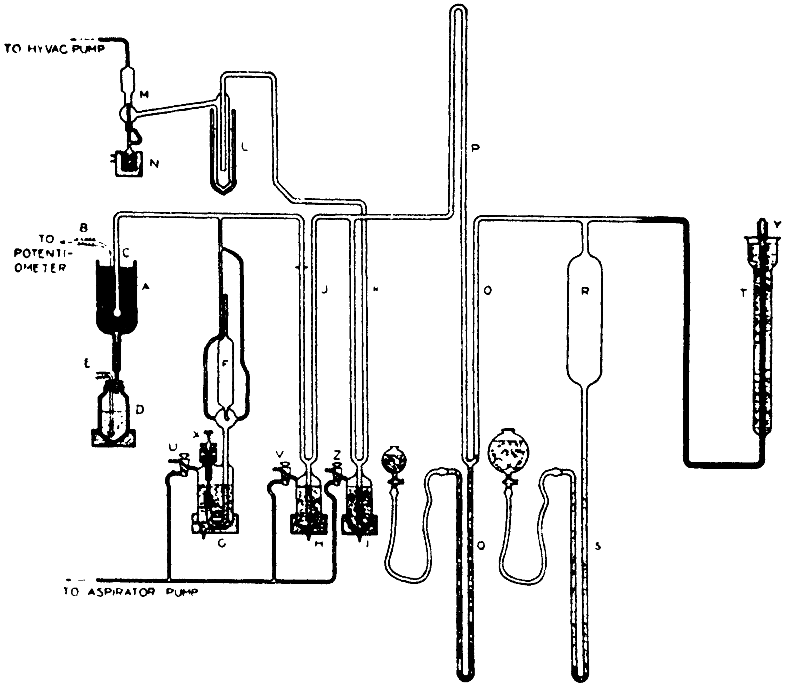
[46] J. J. S. Sebastian and H. C. Howard, *Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 172; *Brit. Chem. Abs.* A. 1934, 743; *Chem. Abs.*, 1934, 28, 3682; *J. Inst. Pet. Tech.*, 1934, 20, 443A.



Courtesy Industrial and Engineering Chemistry

FIG. 282.—Apparatus for Microanalysis of Gaseous Mixtures by Use of Pressure-Temperature Curves. (J. J. S. Sebastian and H. C. Howard)

A. Dewar flask with vacuum-jacketed tube connection
B. Copper-constantan thermocouple in direct contact with freezing bulb
C. Copper-jacketed freezing tube placed in 2-mm.-thick copper shield
D. Lower Dewar flask containing liquid nitrogen
E. Electric heating coil in series with rheostat and ammeter
F. McLeod gage
G, H, I. Mercury reservoirs
J, K, O. Mercury cut off tubes
L. Liquid nitrogen trap
M. Mercury vapor pump
N. Electric heater
P. Connecting U-tube
Q, S. Mercury-filled U-tubes
R. Expansion bulb
T. Sampling reservoir
U, V, Z. Two-way stopcocks for connection with atmosphere or suction
X. Screw for closing off reservoir from McLeod gage
Y. Ground glass stopper for holding weights

The procedure consists in condensing 1 ml. (cc.) of the gas under analysis in a bulb cooled by liquid nitrogen. (See Fig. 282.) The apparatus is evacuated to 10^{-5} mm. and the temperature of the liquid nitrogen slowly raised, about 0.4° to 0.6°C. per minute. The temperature and pressure are read at frequent intervals and plotted against each other. From these data the composition of the gases may be estimated. One of the limitations of the system is said to be in the fact that it has not been possible to determine saturated and unsaturated hydrocarbons of the same number of carbon atoms when both are present in the gas specimen.

An explanation for the rather widely separated boiling points of methane and ethane, when compared with each other and with the remaining members of this homologous series, has been offered by Cox.[47] The reasons given for believing that methane and ethane are not homologous with other hydrocarbons of the paraffin series with regard to boiling point are:

1. Methane contains a carbon-hydrogen bond of unique strength not found elsewhere in the series.
2. Ethane contains a carbon-carbon bond also of unique strength not found elsewhere in the series.
3. Propane contains no bonds that are not duplicated in the higher members of the series.

If methane and ethane are treated as separate problem entities, it is stated that the remainder of the normal paraffin series can be related by the equation:

$$\log B = 1.07575 + 0.949128 \log m - 0.101 \log^2 m$$

where B is the normal boiling point in °K. (assuming 0°C.=273.16°K.), m is the approximate molecular weight, and the logarithms are to base 10.

LOW-TEMPERATURE FRACTIONATION METHODS

Among the outstanding advances in the analysis of complex hydrocarbon mixtures by physical methods is the development of efficient fractionating columns capable of being used for the precise fractional distillation of small quantities of hydrocarbon liquids at temperatures down to the boiling point of liquid nitrogen. The types of apparatus which have been recommended for this procedure include those of Podbielniak, Frey and Yant, Davis, Schaufelberger, MacGillivray and Rosen and Robertson.[48] The Podbielniak apparatus consists essentially of a vacuum-jacketed fractionating column designed for high efficiency at reflux temperatures below atmospheric, together with an accessory apparatus for introducing gas or liquid samples into the column and for temperature and volume measurement. Refrigerants such as liquid air, liquid carbon dioxide, brine, water and compressed air are employed to give the proper reflux ratio. In the column suggested by Frey and Yant controlled reflux was obtained by regulated heat withdrawal from the uppermost 10 cm. of a 50 cm. fractionating column. The effect was accomplished by cooling with liquid air through a 1 mm. annular space filled with hydrogen, whose pressure could be regulated. In this manner the rate of cooling could be controlled. The column described by Davis consists of glass tubing bent into a low pitch spiral of 30 to 40 turns. An immersion-type electrical heating device and a cooled receiver for condensation of the distillate vapors are employed. Schaufelberger advocates a reflux chamber separate from the fractionating column in an apparatus similar to that of Podbielniak. According to MacGillivray, a variable-pressure hydrogen buffer will efficiently control the reflux ratio when the refrigerant is liquid nitrogen. The latter substance will not form explosive mixtures with hydrocarbons in the event of a leak as will liquid air. Rosen and Robertson point out that a column is not necessary in routine analysis of ternary mixtures but that the pressure and temperature of a vaporizing mixture may be plotted and the composition estimated by comparison with a master graph.[49]

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[47] E. R. Cox, *Ind. Eng. Chem.*, 1935, 27, 1423; *J. Inst. Pet. Tech.*, 1936, **22**, 44A; *Chem. Abs.*, 1936, **30**, 1277; *Brit. Chem. Abs.* **A**, 1936, 149.

[48] For a description of the apparatus and procedure for analysis, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. See also H. M. Stanley, *Proc. World Petroleum Congr., London*, 1933, **2**, 830; *J. Inst. Pet. Tech.*, 1934, **20**, 243A; *Brit. Chem. Abs.* **B**, 1934, 741; *Chem. Abs.*, 1934, **28**, 4871. W. A. McMillan, *J. Inst. Pet. Tech.*, 1936, **22**, 616; *J. Inst. Pet. Tech.*, 1936, **22**, 496A; *Chem. Abs.*, 1936, **30**, 8586.

Lang[50] has described a modification of the Podbielniak apparatus which is reported to be efficient for the analysis of gas mixtures containing nitrogen, oxygen, hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, ethane, propene and propane. The sample was introduced into a distilling flask, and any components not condensable at the temperature of liquid air and atmospheric pressure were pumped off into a 100 cc. burette.

For receiving the fractions from the distillation a special 100 cc. burette was used. The burette, instead of being fitted with a compensator tube, was connected at the bottom through a side tube to an auxiliary leveling tube of the same base as the burette and located parallel to the burette. This leveling tube was enclosed in a water jacket. At the top the auxiliary leveling tube extended considerably above the gas burette and was open to the atmosphere, serving as a manometer to indicate the pressure of the gas in the burette with respect to the atmosphere. At the bottom the gas burette was also connected through a stopcock to a leveling tube. During the distillation a three-way stopcock at the top of the gas burette connected the latter to the distillation column. In this manner the auxiliary leveling tube in connection with the burette served as a manometer to show the distillation pressure. The rate of distillation can be controlled by opening the stopcock at the lower end of the gas burette. By regulating the reflux in the column the mercury in the gas burette and in the auxiliary leveling tube could be kept at the same level.

When a fraction was to be separated, or when the burette was full, the three-way stopcock at the top of the burette was closed, the distillation interrupted by cooling and the volume read. The three-way stopcock was then opened to a mercury filled gas-sampling tube and the distillate transferred.

The cut made at the ethylene boiling point range of the distillation curve (—115°C.) was said to contain hydrogen, carbon monoxide, nitrogen, methane and ethylene. This fraction was further analyzed by absorption and combustion, as described previously. The next cut was made between the ethane (—98°C.) and propene (—61°C.) boiling point ranges. The difference in boiling points should be sufficient to give a sharp break in the distillation curve, but in some cases it was necessary to add ethane to the sample to secure a clear ethane fraction which could further be separated into an ethylene-ethane portion and one of ethane-propene. The third cut contained the remainder of propene, propane and any higher homologues.

Eucken and Knick[51] proposed a method for the microanalytical separation of low-boiling hydrocarbons, based upon adsorption of their vapors by activated charcoal. The latter is contained in one arm of a U-tube, which is cooled to —103°C. by liquid ethylene. The tube is then slowly raised into an electrically heated furnace at 250°C. The gases which are evolved are continuously withdrawn from the other arm of the tube by a mercury pump and conducted to a collecting vessel. The pressures in the U-tube and collecting vessel, respectively, are read at frequent intervals and recorded as functions of the time of desorption. The gases are removed from the tube successively, the point at which each constituent is completely removed being marked by a minimum value of pressure in the tube. The proportions of constituents are then determined from the values for the pressure in the collecting vessel which correspond to the minimum values in the tube. The method has been reported as successful in the quantitative determination of a mixture of methane, ethylene, ethane and propane.

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[49] For a method of calculating a master graph, see J. Houpel and D. W. Robertson, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 323; *Chem. Abs.*, 1934, **28**, 6990; *Brit. Chem. Abs.* **B**, 1934, 995.

[50] J. W. Lang, *Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 150; *Brit. Chem. Abs.* **B**, 1935, 612; *J. Inst. Pet. Tech.*, 1935, **21**, 373A; *Chem. Abs.*, 1935, **29**, 4694. See also A. I. Dintzes, *Khim. Tverdogo Topliva*, 1933, **4**, 381; *Chem. Abs.*, 1934, **28**, 5780; *Brit. Chem. Abs.* **B**, 1935, 54.

[51] A Eucken and H. Knick, *Brennstoff-Chem.*, 1936, 17, 241; *Brit. Chem. Abs.* **B**, 1936, 774.

AZEOTROPIC MIXTURES IN LOW-TEMPERATURE FRACTIONATION

The development of precision methods for the analysis of complex hydrocarbon gases obviously is fraught with considerable difficulty. This is true especially in the separation of ethylene from ethane by low-temperature fractional distillation methods.[52] In some instances further fractionation of this cut very often resulted in the isolation of an azeotropic mixture of acetylene and ethane of minimum boiling point. According to McMillan, a mixture containing 70 per cent of ethane and 30 per cent of acetylene distilled at —94.5°C. until 73.5 per cent had come over, at which point the temperature broke sharply to —83.3°C., and the remainder of the ethane distilled at that temperature. With 70 per cent acetylene and 30 per cent ethane, a distillate amounting to 50.2 per cent of the mixture came over at —94.5°C., at which point the fractionating column froze solid with acetylene. When analyzed by catalytic hydrogenation of the acetylene over a reduced nickel catalyst, each of the azeotropic mixtures boiling at —94.5°C. gave 40.8 per cent of acetylene and 59.2 per cent of ethane. Additional determinations on five other samples gave a boiling point range of —94.5 ± 0.1°C. and a composition range of: acetylene, 40.75 ± 0.25 per cent; ethane, 59.25 ± 0.25 per cent for the azeotropic mixture. These results offer an explanation for the presence of acetylene as shown by tests with various reagents even though no acetylene had been observed on fractional distillation of the sample. It is also reported to explain at least in part the appearance of so-called "carbon dioxide plugs" which develop from time to time in distillation apparatus although the gases have been previously scrubbed with fresh caustic. The white solid which separates in such cases is usually not carbon dioxide but acetylene, which can be identified by Lebeau's reagent (mentioned in the section in this chapter on absorption).

Azeotropic mixtures have been employed in some cases to effect the separation of otherwise difficultly divided hydrocarbon portions. For example, the practical fractionation of a mixture of hydrocarbons having 4 carbon atoms to the molecule into a butene cut and a butane cut by distillation is said to be very difficult.[53] This is due to the small boiling point range (see Table 210).

TABLE 210.—*Boiling Points of Butanes and Butenes.*

	B.P., °C.		B.P., °C.
Isobutane	−12.4	*n*-Butane	−0.6
Isobutene	− 6.7	2-Butene (*trans.*)	1.0
1-Butene	− 6.7	2-Butene (*cis*)	3.7

Moreover, the order of the hydrocarbons with respect to boiling point necessitates obtaining 4 fractions instead of 2.

Separation is reported to be more readily effected by distillation in the presence of sulphur dioxide which forms azeotropic mixtures with the minimum boiling points at atmospheric pressure shown in Table 211.

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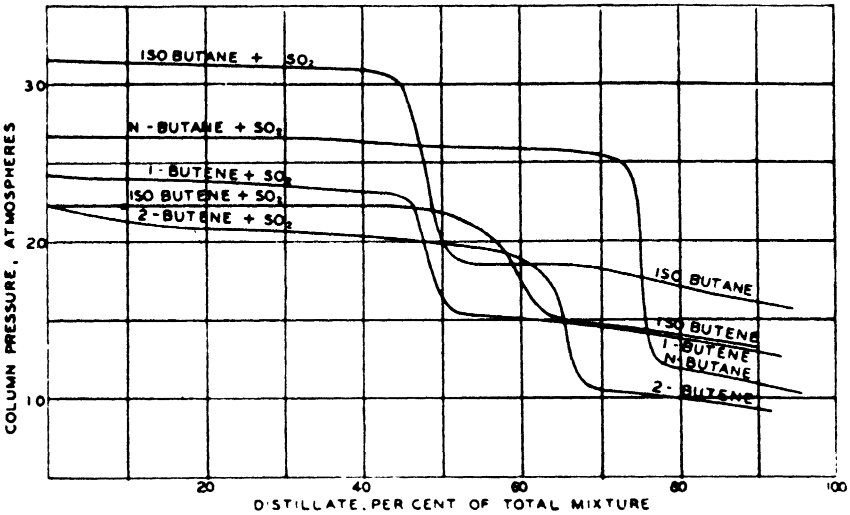
[52] W. A. McMillan, *J.A.C.S.*, 1936, **58**, 1345; *Chem. Abs.*, 1936, **30**, 6702.

[53] M. P. Matuszak and F. E. Frey, *Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 111; *Chem. Abs.*, 1937, **31**, 3755; *Brit. Chem. Abs.* A (2), 1937, 173.

TABLE 211.—*Boiling Points of Azeotropes of Butanes and Butenes.*

Azeotrope	B.P., °C.	Azeotrope	B.P., °C.
Isobutane	−27	Isobutene	−17
n-Butane	−21	2-Butene (mixture of *cis* and *trans* forms)	−16
1-Butene	−18		

The order of the azeotropes with respect to boiling point differs from that of the hydrocarbons themselves for both the butane azeotropes are said to have boiling points lower than any butene azeotropes. If sulphur dioxide is added to a mixture of 4 carbon hydrocarbons in amounts equivalent to the azeotropes of the butanes present which lies between 59 and 62 per cent for cracked or cracking gas, and if the resulting mixture is then fractionally distilled, the butanes can be separated from the butenes. In this manner azeotropic mixtures of the butanes are formed, boiling between −27° and −21°C., while the butenes do not form azeotropes and boil between−6.7° and 3.7°C. Thus there is a difference of about 14°C. between the highest boiling paraffin azeotrope and the lowest boiling olefin.



Courtesy Phillips Petroleum Co.

FIG. 283.—Typical Isothermal Distillation Curves for Binary Mixtures of Sulphur Dioxide with Butanes and Butenes at 3°C. (M. P. Matuszak and F. E. Frey)

DETERMINATION OF UNSATURATED HYDROCARBONS IN GAS MIXTURES

The quantitative estimation of unsaturated hydrocarbons in gas mixtures likewise seems to be a matter of some difficulty, and can only be effected in few cases without some method of fractionation. Attention has been given to the analysis of olefin mixtures by absorption in various concentrations of sulphuric acid, with or without the addition of metallic salts. With sulphuric acid of appropriate concentration it is possible to effect an analytical separation of ethylene from its higher homologues because ethylene is absorbed with most difficulty by sulphuric acid. However, the rates of absorption of propene and the two straight-chain butenes approach one another so closely that any analytical separation of them by this acid seems to be rather impracticable.

Determination of the total amount of unsaturated hydrocarbons in a gas mixture is identical with the problem of complete absorption of the ethylene which takes place only after a relatively long time, while the other unsaturated hydrocarbon gases require contact periods of much shorter duration. Bromine and fuming sulphuric acid are the reagents usually employed for this purpose.[54] Of the two, bromine water is reported to be more efficient, especially if the operation is carried out in a darkened pipette. Fuming sulphuric acid rapidly absorbs all unsaturated hydrocarbons, including ethylene, but simultaneously paraffin hydrocarbons also.

ABSORPTION OF OLEFINS BY SULPHURIC ACID OF VARIOUS CONCENTRATIONS

A number of methods have been proposed for the preferential absorption of various individual olefins by treatment with sulphuric acid of different concentrations. It has been suggested that 87 per cent sulphuric acid activated by silver and nickel sulphates be used for ethylene, 83 to 84 per cent acid for propene and 63 to 64 per cent acid for isobutene.[55]

Tropsch and Mattox[56] have described a method for estimating ethylene, propene and butene in cracked refinery gases. Propene and butene are estimated by a method which consists essentially in determining the molecular weight of the original gas sample (dry and free of carbon dioxide and hydrogen sulphide) and also after the removal of propene and butene by 87 per cent sulphuric acid. These values are obtained with a Stock electromagnetic gas balance mentioned previously in this chapter. From the change in the molecular weight of the gas on the removal of propene and butene by the acid and the volume per cent of propene and butene removed, the molecular weight of these olefins is calculated and also the volume per cent of propene and of butene in the original mixture is computed. Ethylene is determined (after removal of other olefins) by absorption in a mixture comprising 1 to 15 per cent of concentrated sulphuric acid saturated with nickel sulphate at 20°C. and concentrated sulphuric acid containing 0.6 per cent of silver sulphate. The apparatus consists of a gas burette connected to a Stock electromagnetic gas balance and to two absorption bulbs (Fig. 284). One-half of a 200 cc. sample is used for the molecular weight determination, while the other 100 cc. is treated to remove the propene and butene simultaneously.

When ethylene is to be employed in the preparation of ethyl alcohol, it may be necessary to remove the higher olefins. According to Sakmin and Michnovska[57] the propene content of a gas mixture may be determined by absorption in sulphuric acid. In this method 80 cc. of the gas under analysis is forced into a gas burette and treated with 30 cc. of 87 per cent sulphuric acid. If less than 10 per cent of propene is present, the absorption is said to be complete in 10 minutes.

ANALYSIS OF GASEOUS UNSATURATED HYDROCARBONS BY BROMINATION

Two general methods for the addition of bromine to olefins and diolefins have been reported. The first consists of mixing the gaseous hydrocarbon mixture with bromine water, the second of treating the gas under analysis with potassium bromate, potassium bromide and sulphuric acid.[58] The three latter substances evolve bromine slowly according to the mechanism:

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[54] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

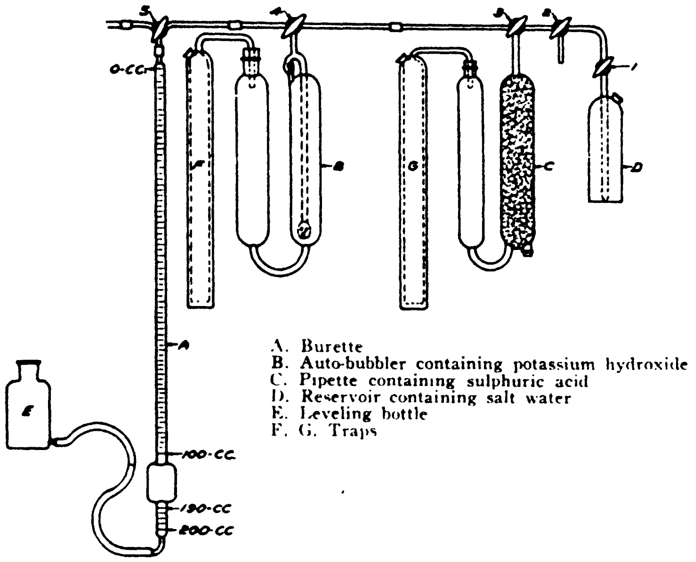
[55] Carleton Ellis, *loc. cit.*

[56] H. Tropsch and W. J. Mattox, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 404; *Chem. Abs.*, 1935, **29**, 319; *Brit. Chem. Abs.* **B**, 1935, 392. See also M. B. Markovich and M. I. Dement'eva, *Materials on Cracking and Chemical Treatment of Products Obtained, Khimteoret (Leningrad)*, **1935**, No. 2, 131; *Chem. Abs.*, 1935, **29**, 5778. E. A. Andreev and M. B. Neiman, *J. Applied Chem.* (*U.S.S.R.*), 1935, **8**, 1100; *Chem. Abs.*, 1936, **30**, 5464.

[57] P. K. Sakmin and L. Michnovska, *Z. anal. Chem.*, 1935, **100**, 264; *Brit. Chem. Abs.* **B**, 1935, 442; *Chem. Abs.*, 1935, **29**, 3262.

$$KBrO_3 + 6KBr + 3H_2SO_4 \longrightarrow 3K_2SO_4 + 3H_2O + KBr + 3Br_2$$

The halogen thus produced adds directly to the unsaturated gases forming dibromides with monolefins and tetrabromides with diolefins.



A. Burette
B. Auto-bubbler containing potassium hydroxide
C. Pipette containing sulphuric acid
D. Reservoir containing salt water
E. Leveling bottle
F, G. Traps

Courtesy Industrial and Engineering Chemistry

FIG. 284.—Apparatus for Determination of Propene and Butene in Gaseous Mixtures. (H. Tropsch and W. J. Mattox)

The first method, that is, determination of olefins by the use of bromine water, is said to be attended with some difficulties.[59] Among these are:

1. If the gas contains a high percentage of unsaturated hydrocarbon gases, it is difficult on account of the slow diffusion of bromine vapors to get the latter sufficiently mixed with the gas to react completely with the olefins present.
2. When mercury is used as the confining liquid in the gas burette it is necessary to avoid contact of bromine fumes with this metal.
3. When the percentage of paraffins in the sample is high, the solubility of these gases in bromine water is sufficiently great to introduce serious errors in the determination of small amounts of olefins.
4. When excess bromine vapors are removed by absorption in sodium or potassium hydroxide after reaction with olefins, the evolution of oxygen by decomposition of the hypobromite formed must be avoided.

The investigator reported that these difficulties can be overcome to a large degree by employing a solution saturated with both sodium chloride and bromine instead of bromine water as the absorbing medium. In this manner the absorption of paraffins was said to be reduced to a negligible amount. A pipette containing 25 per cent caustic soda was attached to the bulb containing the absorbing solution. The caustic soda was placed in the apparatus to remove bromine fumes. The procedure consisted of bubbling the gas through the bromine solution, if the concentration of olefins was high. If low, part of the gas was bubbled through the solution and the remainder conducted into the excess bromine fumes, the object being to expose only a small quantity of the gas to the solution and at the same time to insure excess bromine in the gas. The brominated gas is then drawn through the caustic soda pipette by suction and forced through a tube to a caustic potash solution. In this way the excess bromine vapors are removed. To minimize the error caused by evolution of oxygen in the caustic soda pipette, fresh reagent was added frequently.

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[58] See, Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, **1934**.

[59] J. W. Lang, *Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 150; *Chem. Abs.*, 1935, **29**, 4694; *Brit. Chem. Abs.* **B**, 1935, 612. *Cf.* P. K. Sakmin, *Gas u. Wasserfach*, 1935, **78**, 490; *Brit. Chem. Abs.* **B**, 1935, 789; *Chem. Abs.*, 1935, **29**, 6732.

Winbladh[60] suggests that cracked petroleum gases be treated with bromine water at —20 to —30°C. to form dibromides and tetrabromides, respectively, of the monolefins and diolefins present. The bromination products are collected in ice-cooled 10 per cent potassium bromide solution and distilled under 15 mm. pressure to separate the dibromides of ethylene, propene and butene from those derived from higher olefins. The residue, which contains the diolefin tetrabromides (as well as the higher dibromides), is agitated with hot ethyl alcohol. On cooling the mixture to 0°C. crystals of butadiene tetrabromide are said to be obtained. One portion of the distillate on shaking with a solution of disodium thioglycolate forms crystals of ethylenebisthioglycolic acid which may be dried and weighed. A second portion of this distillate is again fractionated into two cuts, the first boiling below 44°C. under 15 mm., the second boiling between 44 and 55°C. under 15 mm. The fractions were then treated with alcoholic disodium thioglycolate and caustic soda. The olefins other than ethylene may then be estimated by adding potassium bromate, potassium bromide and sulphuric acid to the two cuts from the last distillation. Excess bromine is replaced by iodine from potassium iodide and the iodine titrated with sodium thiosulphate. The process is reported to be tedious, four days being required for a complete determination. In addition, the error in estimating the olefins other than ethylene is said to be as high as 5.5 per cent.

Mulliken and Wakeman[61] point out that the bromide-bromate titration may be applied to the determination of mono- and diolefins. In their procedure they recommend that the calculated amount[62] of standardized bromide-bromate solution be placed in a glass-stoppered flask and mixed with 0.5 cc. of the hydrocarbon mixture. Then 15 cc. of 10 per cent sulphuric acid are incorporated. The bottle is stoppered and shaken until the bromine color vanishes. Instead of disappearing, should a visible bromine color still remain after two minutes of shaking, 5 cc. of 15 per cent potassium iodide are added and the liberated iodine titrated with 0.2N thiosulphate solution. If the color of the bromine disappears additional aqueous bromide-bromate is added until a yellow color persists in the solution. Potassium iodide is incorporated and the liberated iodine titrated with sodium thiosulphate.

Special Methods of Analysis of Unsaturated Gases

For the determination of acetylene in gases which contain high percentages of that substance, Novotny[63] suggested that the mixture be treated with silver

[60] R. Winbladh, *Ing. Vetenskaps, Akad. Handl.*, 1936, **138**; *Chem. Abs.*, 1936, **30**, 3746; *Brit. Chem. Abs.* **B**, 1936, 732.

[61] S. P. Mulliken and R. L. Wakeman, *Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 59; *Chem. Abs.*, 1935, **29**, 1362; *Brit. Chem. Abs.* **A**, 1935, 324.

[62] To the observed boiling point of the hydrocarbon mixture, 25°C. was added. The amount of bromide-bromate solution theoretically necessary to titrate an olefin boiling at such a temperature was calculated. This quantity of bromide-bromate solution minus 2 cc. is employed. Hence, less than the amount theoretically necessary for the hydrocarbon at hand was always used at the beginning.

[63] D. F. Novotny, *Collection Czechoslov. Chem. Communications*, 1935, 7, 84; *Brit. Chem. Abs.* **B**, 1935, 394; *Chem. Abs.*, 1935, **29**, 3940.

nitrate to form a precipitate of the silver nitrate complex of silver acetylide ($C_2Ag_2NO_3$). The latter is filtered off and the excess silver nitrate titrated with 0.1N ammonium thiocyanate or determined gravimetrically as silver chloride.

A method for the estimation of gaseous olefins by catalytic hydrogenation has been proposed.[64] It requires that a measured volume of hydrogen be mixed with a known quantity of olefin-containing gas and the mixture passed over an appropriate catalyst at 20°C. and 1 atmosphere pressure. The resulting contraction in volume is a direct measure of the amount of olefin present.

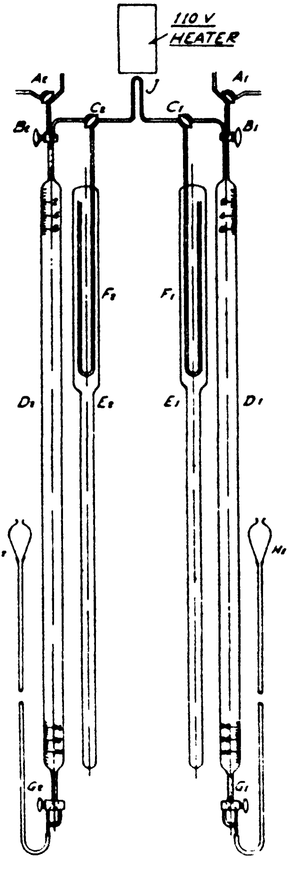

FIG. 285.
Diagram of Apparatus for Analysis of Olefinic Gases.
(W. A. McMillan, H. A. Cole and A. V. Ritchie)

Courtesy Texas Co.

A_1, A_2. Tubes for introducing samples
D_1, D_2. Burettes
F_1, F_2. Manometers
H_1, H_2. Leveling bottles
J. Catalyst tube

Courtesy Industrial and Engineering Chemistry

$$C_nH_{2n} + H_2 \longrightarrow C_nH_{2n+2}$$

One volume of olefin reacts with 1 volume of hydrogen to form 1 volume of paraffin, and the change in volume on hydrogenation is from 2 volumes to 1. In the case of diolefins, the contraction is represented by:

$$C_nH_{2n-2} + 2H_2 \longrightarrow C_nH_{2n+2}$$

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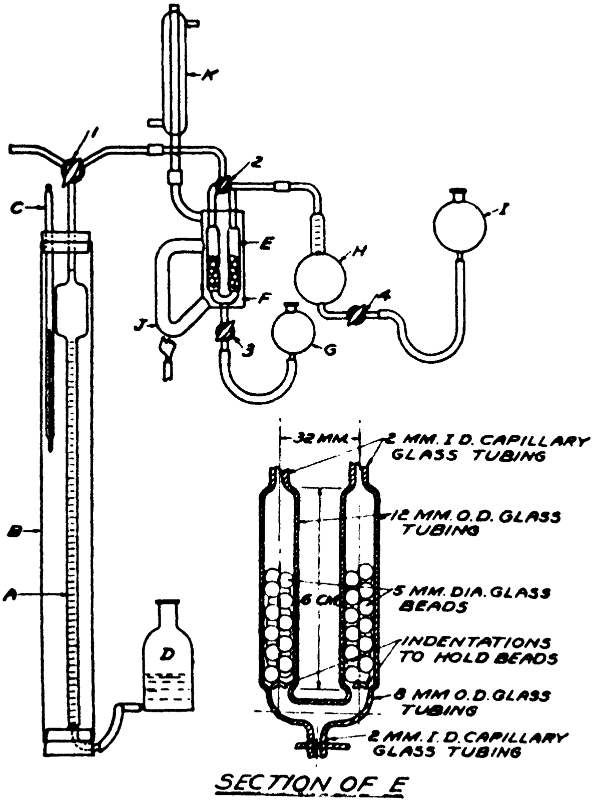
[64] W. A. McMillan, H. A. Cole and A. V. Ritchie, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 105. *Brit. Chem. Abs.* **B**, 1936, 435; *J. Inst. Pet. Tech.*, 1936, **22**, 301A. See also, K. P. Lavrovskii, A. F. Nikolaeva, P. V. Puchkov and G. M. Freiman, *Neft. Khoz.*, 1935, **28** (8) 65, (9), 75; *Chem. Abs.*, 1936, **30**, 8588. W. J. C. de Kok, H. I. Waterman and H. A. van Westen, *J.S.C.I.*, 1936, **55**, 225T; *J. Inst. Pet. Tech.*, 1936, **22**, 438A; *Chem. Abs.*, 1936, **30**, 7929.

The catalyst employed in such hydrogenations consisted of nickel saturated asbestos, prepared from nickel nitrate hexahydrate, asbestos and nitric acid. The apparatus consists of two water-jacketed burettes and compensators with a catalyst tube mounted between them (Fig. 285). The gases are measured, conducted over the catalyst and the contraction in volume noted.



A. Burette
B. Water jacket
C. Thermometer
D. Leveling bottle
E. Absorber
F. Water jacket
G. Leveling bulb
H. Gas bulb
I. Leveling bulb
J. Heating tube
K. Reflux condenser

Courtesy Industrial and Engineering Chemistry

FIG. 286.—Gas Burette and Absorption Tube Employed in Determination of Butadiene in Gas Mixtures. (H. Tropsch and W. J. Mattox)

According to Dillon, Young and Lucas[65] mixtures of the three normal butenes can be analyzed by means of the densities of their dibromides and the reaction rate of these latter compounds with potassium iodide. The method depends on the fact that each of the three butenes is quantitatively converted to the dibromide by treatment with bromine, and each of the dibromides has a different second-order reaction rate with potassium iodide in methanol at 75°C. A combination of the reaction rate with the density is sufficient for the analysis of any mixture of the three dibromides, and from this the content of the three butenes can be computed. To investigate the possibility of the dibromide mixture undergoing isomerization during the reaction with potassium iodide, the stability of these substances was tested by distillation at atmospheric pressure.[66] A sample of 111.5 g. of dibromobutane, containing the three types and having n_D^{25} 1.5118, reaction rate constant (with potassium iodide) 0.0600 and $d_4^{25} = 1.7835$, was reported to distil between 159-165°C., leaving no high boiling residue. The distillate was found to have n_D^{25} 1.5118, reaction rate constant 0.0598 and d_4^{25} 1.7828. The absence of change in the reaction rate constant was said to show that no isomerization had occurred. Traces of decomposition products due to the loss of hydrogen bromide were reported as the cause of the slight change in density, but it was stated that a distillation at reduced pressure would restore the density to its previous value.

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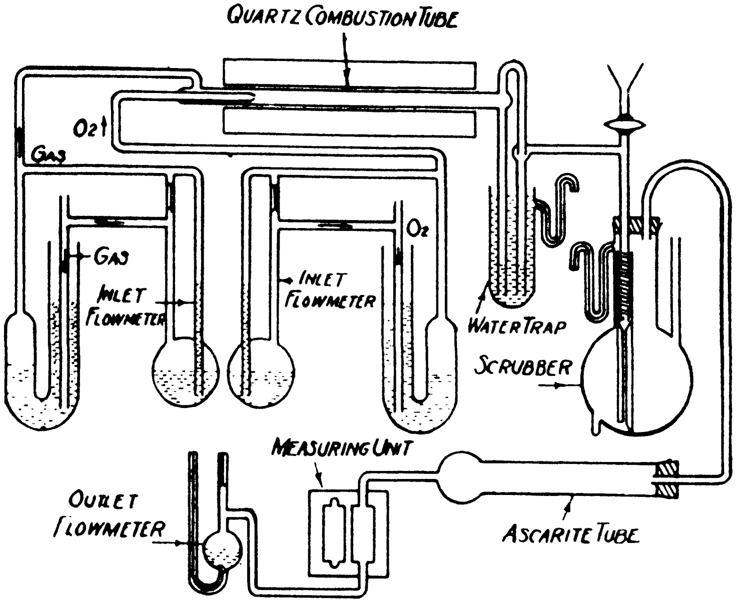
[65] R. T. Dillon, W. G. Young and H. J. Lucas, *J.A.C.S.*, 1930, **52**, 1953; *Chem. Abs.*, 1930, **24**, 2979; *Brit. Chem. Abs.* **A**, 1930, 888.



Courtesy U. S. Bureau of Mines

FIG. 287.—Apparatus for Continuous Determination of Helium in Natural Gas by Thermal-Conductivity Measurement. (A. S. Smith)

Tropsch and Mattox[67] suggest the use of maleic anhydride for the estimation of butadiene. The reaction between these two substances is said to be rapid at 100°C., which would seem to point out an advantage in using the molten anhydride. The apparatus consisted of a gas burette in connection with an absorption tube. (See Fig. 286.) Boiling water was circulated about the absorption pipette to maintain the temperature at 100°C. The gas was forced through the absorbent twice and the diminution in volume noted. It is stated that the anhydride does not absorb olefins or acetylene if the concentration of the latter is less than 40 per cent.

The use of a Wheatstone bridge for the determination of helium and argon in natural gas is proposed by Gerling.[68] The gases were heated by two wires of the bridge and the change in thermal conductivity noted. The pressure, if it is above 40 mm., is said to have no effect upon the thermal conductivity or resistance. The apparatus was originally calibrated with pure gases and is reported to be sensitive to 0.3 per cent of helium in a sample. To remove the hydrocarbons which are present, measured volumes of natural gas and oxygen are mixed and the hydrocarbons separated by combustion.[69] In the procedure natural gas was led through an inlet flow meter at one l. per hour at 0°C. and 760 mm., while oxygen entered at 1.685 l. per hour under the same conditions. The two were admixed and conducted at a space velocity of 0.27 to 0.69 cc. per hour per cc. of reaction space through a quartz combustion tube. The latter contained cobalt oxide at 800°C. As the gases leave the combustion chamber, condensed water vapor is removed in a water trap, and carbon dioxide by scrubbing with caustic soda and ascarite.[69a] The gas, in which the concentration of helium has been increased, is then analyzed by thermal-conductivity measurement.

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[66] W. G. Young and S. Winstein, *J.A.C.S.*, 1936, **58**, 102; *Brit. Chem. Abs.* **A**, 1936, 310; *Chem. Abs.*, 1936, **30**, 2136.

[67] H. Tropsch and W. J. Mattox, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 104; *Brit. Chem. Abs.* **B**, 1934, 390; *J. Inst. Pet. Tech.*, 1934, **20**, 488A; *Chem. Abs.*, 1934, **28**, 3029. See also, Carleton Ellis, "The Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, 1935.

Benzene vapors may be determined colorimetrically. The sample of gas under analysis is treated with concentrated nitric acid to form *m*-dinitrobenzene. The mixture is neutralized and the nitrated benzene extracted with butanone. When caustic soda is added to the dinitrobenzene extract a violet color is reported to be produced, which may then be matched against known color standards.[70]

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[68] E. K. Gerling, *J. Applied Chem. (U.S.S.R.)*, 1933, **6**, 1153; *J. Inst. Pet. Tech.*, 1934, **20**, 567A; *Brit. Chem. Abs.* **B**, 1934, 269; *Chem. Abs.*, 1934, **28**, 3872. *Cf.* W. J. Willenborg, British P. 424,053, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 164A; *Chem. Abs.*, 1935, **29**, 5254; *Brit. Chem. Abs.* **B**, 1935, 363.

[69] A. S. Smith, *Bur. Mines, Rept. of Investigations*, **1934**, No. 3250; *Chem. Abs.*, 1934, **28**, 6594; *Brit. Chem. Abs.* **B**, 1935, 186.

[69a] Ascarite is a mixture of alkali and asbestos. See J. B. Stetser, *Chemistry and Industry*, **1924**, 637. J. B. Stetser and R. H. Norton, *Iron Age*, 1918, **102**, 443; *Chem. Abs.*, 1918, **12**, 2076.

[70] H. H. Schrenk, W. P. Yant and S. J. Pearce, *Bur. Mines Rept. of Investigation*, **1935**, No. 3293; *Chem. Abs.*, 1935, **29**, 7869; *Brit. Chem. Abs.* **B**, 1936, 178.

Chapter 50

Analysis of Petroleum Distillates

Petroleum oils consist of extremely complex mixtures of hydrocarbon material together with smaller amounts of organic compounds containing, e.g., nitrogen and sulphur, and still smaller proportions of inorganic substances (See Chapter 1). During the course of refining operations, it is usual to remove almost all of the non-hydrocarbon substances since these are considered present as impurities which are held to be injurious in the commercial products. It is convenient to treat the methods used in the quantitative evaluation of these different substances first and then proceed to a consideration of the measurement and significance of physical characteristics of petroleum fractions.[1]

HYDROCARBON ANALYSIS

As has been pointed out in Chapter 1, the petroleums obtained from different portions of the world differ in their composition to a considerable extent. One of the principal differences is in the type of the predominant hydrocarbons. Thus, the oils from Baku and Grozny contain a high proportion of naphthenic constituents whereas oils from Pennsylvania are very largely paraffinic. On the other hand, aromatic hydrocarbons seem to be the characteristic components of petroleums from Borneo. Olefins apparently do not occur to any appreciable extent in crude petroleum, although they may form as much as 60 per cent of the gasoline resulting from vapor phase cracking.[2] Because of the influence of these various types of hydrocarbons on the uses and properties of petroleum and its fractions, it is of importance to differentiate between them and to estimate their relative proportions in any given distillate. The problems presented in these distinctions are rendered more difficult by the complexity of the petroleum itself and the variation in reactivity of the different members of any homologous series.

Polyakin[3] has described a method by which he determines quantitatively the alkenes, aromatics, six- and five-carbon-ring-naphthenes and paraffins in gasoline.

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[1] See also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. D. A. Howes, *J. Inst. Pet. Tech.*, 1930, **16**, 54; *Brit. Chem. Abs.* **B**, 1930, 802; *Chem. Abs.*, 1930, **24**, 4381. J. S. S. Brame, *J. Inst. Pet. Tech.*, 1933, **19**, 652; *Chem. Abs.*, 1933, **27**, 4912. W. H. Thomas, *ibid.*, 636; *Chem. Abs.*, 1933, **27**, 4912. C. Chilvers, *ibid.*, 1934, **20**, 457; *Chem. Abs.*, 1934, **28**, 5641; *J. Inst. Pet. Tech.*, 1934, **20**, 449A. A. R. Bowen, *ibid.*, 419; *Chem. Abs.*, 1934, **28**, 4581. B. Blajot, *Pol. farm. mil.*, 1931, **9**, 225; *Chim. et ind.*, 1931, **26**, 1074; *Chem. Abs.*, 1932, **26**, 1425. E. Hubendick, *Tek. Fören. i Finland Förhandl*, 1931, **51**, 99, 148, 183, 221; *Chem. Abs.*, 1931, **25**, 5975. H. Schildwächter and H. Martin, *Brennstoff-Chem.*, 1935, **16**, 301; *Brit. Chem. Abs.* **B**, 1935, 980; *Chem. Abs.*, 1936, **30**, 3963. B. Hilliger, *Proc. World Petr. Congr. London*, 1933, **2**, 431; *J. Inst. Pet. Tech.*, 1934, **20**, 313A (*Cf. Petroleum Z.*, 1930, **26**, *Motorenbetrieb und Maschinen-Schmierung*, **1930**, No. 5, 3; No. 6, 9; *Chem. Abs.*, 1930, **24**, 4621). E. Kadmer, *Petroleum Z.*, **29**, No. 16, *Motorenbetrieb und Maschinen-Schmierung*, 1933, **6**, No. 4, 2; *Chem. Abs.*, 1933, **27**, 3592. W. B. Hardy, *Dept. Sci. Ind. Research, Lubrication Research* **Tech. Paper, No. 1**, 1 (1930); *Chem. Abs.*, 1930, **24**, 3894. H. H. Langdon, *State Col. of Wash., Engr. Expt. Sta. Bull.*, 1933, **41**; *Chem. Abs.*, 1933, **27**, 4065. M. Brutzcus, *Compt. rend.*, 1935, **201**, 423; *Brit. Chem. Abs.* **B**. 1935, 1031.

[2] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. See also Chapters 1, 2, 3, 4, 5, this text. W. Tiraspolsky (*Petroleum Z.*, 1934 **30**, No. 51, 1; *Brit. Chem. Abs.* **B**, 1935, 301) believes that the condensable constituents in the natural gas from a well should be included in the analysis of crude oils.

[3] Yu. Polyakin, *Neft. Khoz.*, 1935, **28** (8), 74; *Chem. Abs.*, 1936, **30**, 3989; *J. Inst. Pet. Tech.*, 1936, **22**, 143A.

His procedure is to pass the vapors from a weighed sample (0.1 to 0.5 g.) through a series of absorption chambers and combustion tubes in which is maintained an atmosphere of nitrogen. Unsaturates are absorbed by a solution of mercuric acetate, and after drying the residual vapors the aromatic hydrocarbons are removed by sulphuric acid containing silver nitrate. The naphthenes with six-membered rings are dehydrogenated to aromatic hydrocarbons by passage at 300°C. over platinized asbestos. The five-carbon-ring-naphthenes and the paraffins are unaffected by this treatment. The aromatics are absorbed in sulphuric acid, after which the penta-naphthenes and paraffins are adsorbed on activated carbon. The hydrogen from the dehydrogenation on platinized asbestos is burned at 300°C. in a tube containing cupric oxide, and the water absorbed by phosphorus pentoxide.

In addition to methods which depend upon chemical analysis, analyses may be computed from data obtained in simple tests. For example, if v is the volume of unsaturated and aromatic hydrocarbons in a distillate, T the 50 per cent point (°F.) of the residue after treatment with sulphuric acid and d the specific gravity of the distilled residue, the percentage of paraffinic and naphthenic hydrocarbons has been calculated from formulas given by Minter.[4]

$$\text{Paraffin }\% = \frac{\left(1 - \frac{v}{100}\right)(0.7126 + 0.000244T - d)}{(0.0591 + 0.000016T)100}$$

$$\text{Naphthene }\% = \frac{\left(1 - \frac{v}{100}\right)(1 - 0.7126 + 0.000244T - d)}{(0.0591 + 0.000016T)100}$$

Tilicheev and Masina[5] have reported a method for the calculation of aromatic and unsaturated compounds in a gasoline which depends upon the determination of the aniline point before and after treatment with Kattwinkel's reagent (phosphoric and sulphuric acids) and also after treatment with 98 per cent sulphuric acid. Further, the proportion of aromatic compounds may be determined by reacting unsaturates with bromine and separating the portion containing aromatics by distillation. In the latter distillate the aromatics are determined by sulphonation. Using sulphuric acid of specific gravity 1.84 to remove aromatics from 50 cc. of a gas oil, a somewhat similar procedure for the analysis of gas oils has been described by van Dijk.[6] The naphthene content is subsequently calculated by using the specific refraction methods described later in this chapter.

The estimation of aliphatic hydrocarbons in aromatic hydrocarbons, such as commercial benzene, has been outlined by Goettsch.[6a] One volume of the hydrocarbon and 5 volumes of 95 per cent ethanol are mixed. To 30 cc. of this mixture in a 50 cc. bottle, water is added from a burette until separation of the hydrocarbon just takes place. By reference to tables (based on determinations with known mixtures), it is then possible to read off the per cent of aromatics in the original hydrocarbon mixture.

A micromethod for the estimation of the hydrocarbons in cracked gasoline has been proposed by Bespolov and Generalov.[7] This procedure is very similar, in the separate tests used, to the method of Polyakin[8] previously described. The essential differences are that unsaturated compounds are absorbed in bromine dissolved in acetic acid rather than in mercuric acetate solution, and subsequent operations are not carried out in a continuous manner.

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[4] C. C. Minter, *Nat. Pet. News*, 1933, **25**, No. 8, 25, 27; *Chem. Abs.*, 1933, **27**, 2792; *Brit. Chem. Abs.* **B**, 1933, 773; *J. Inst. Pet. Tech.*, 1934, **20**, 152A.

[5] M. D. Tilicheev and M. P. Masina, *Khimicheskii Sostav Neftei i Neftyannikh Productov (A. N. Sakhanov), Moscow-Petrograd*, **1931**, 286; *Neft. Khoz.*, 1932, **23**, 161; *Chem. Abs.*, 1933, **27**, 2024; *Brit. Chem. Abs.* **B**, 1933, 659.

[6] J. A. van Dijk, *Het. Gas*, 1933, **53**, 449; *Chem. Abs.*, 1934, **28**, 885.

[6a] G. Goettsch, *Verfkroniek*, 1933, **6**, 14, 325; *Brit. Chem. Abs.* **B**, 1934, 948; *Chem. Zentr.*, 1934, **1**, 1265; *Chem. Abs.*, 1934, **28**, 3569.

[7] N. E. Bespolov and V. M. Generalov, *Azer. Neft. Khoz.*, **1934**, No. 11-12, 90; *Chem. Abs.*, 1935, **29**, 7628.

THE USE OF ULTRAVIOLET LIGHT IN CLASSIFICATION OF HYDROCARBONS

The use of ultraviolet light in the artificial aging of gasoline and other petroleum fractions has been discussed in Chapter 40. The characteristic fluorescence of different classes of hydrocarbons under the influence of light from either a mercury or iron arc light has been recommended as a possible method for distinguishing between various hydrocarbons and waxes. Generally the fluorescence has not been sufficiently characteristic to permit of the identification of the several compounds studied in mixtures.[9] According to Balada[10] the fluorescence of naphthenic oils is blue, of asphaltic oils brown and of paraffin-base oils a light milky-yellow. He suggested that it would be possible to follow the change from naphthenic (blue fluorescence) to asphaltic (brown fluorescence) substances which takes place during oxidation of insulating or lubricating oils up to an asphalt content of about 0.40 per cent. This method is said to be capable of a reasonable degree of accuracy when applied to oils from the same source.

ESTIMATION OF ALKENES

The quantitative estimation of alkenes (ethylenic hydrocarbons) has been effected by several reactions which are typical of this class of compounds.[11] Among the more usual methods may be mentioned absorption in sulphuric acid,[12] halogenation, reaction with mercuric salts or with other reagents such as ozone, sulphur monochloride[13] and antimony trichloride.[14]

Absorption of alkenes in sulphuric acid is complicated by the fact that acid strong enough to remove polymers of diolefins (which may be present due to the action of the acid) will also extract some of the aromatic hydrocarbons.[15] It is suggested that the proportion of aromatic and olefinic hydrocarbons may be determined collectively by absorption in 98.3 per cent sulphuric acid and individually by absorption of the olefins in a 6 per cent aqueous mercuric acetate solution.[16]

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[8] Yu. Polyakin, *loc. cit.*

[9] E. Galle, R. Klatt and W. Friedl, *Montan. Rundschau*, 1935, **27**, (18); *Chem. Abs.*, 1936, **30**, 427; *Petroleum Z.*, 1935, **31**, No. 36, 1; *Brit. Chem. Abs.* **B**, 1935, 980. See also, S. Bruckner and P. Meinhard, *Petroleum Z.*, 1933, **29**, No. 13, 8; *Chem. Abs.*, 1933, **27**, 3597; *Brit. Chem. Abs.* **B**, 1933, 418.

[10] A. Balada, *Petroleum Z.*, 1935, **31**, No. 48, 11; *Brit. Chem. Abs.* **B**, 1936, 83; *Chem. Abs.*, 1936, **30**, 3211; *J. Inst. Pet. Tech.*, 1936, **22**, 48A.

[11] See Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, **1934**, and this book, Chapters 24 and 25.

[12] A method for evaluation of petrolatum by rubbing with sulphuric acid is described by V. O. Schmatolla, *Pharm. Ztg.*, 1933, **78**, 1214; *Chem. Abs.*, 1934, **28**, 855.

[13] S. S. Nametkin and V. Zaborovskaya, *J. Applied Chem. (U.S.S.R.)*, 1936, **9**, 555; *Chem. Abs.*, 1936, **30**, 7828; *Brit. Chem. Abs.* **B**, 1936, 627. *Cf.* also S. S. Nametkin and E. A. Robinzon, *Neft. Khoz.*, 1933, **24**, 292; *Brit. Chem. Abs.* **B**, 1934, 262; *Chem. Abs.*, 1933, **27**, 5953.

[14] Antimony trichloride has been found to give color reactions with various types of unsaturated compounds. See S. Sabetay, *Compt. rend.*, 1933, **197**, 557; *Chem. Abs.*, 1933, **27**, 5714; *Brit. Chem. Abs.* **A**, 1933, 1138. R. Delaby, S. Sabetay and M. Janot, *Compt. rend.*, 1934, **198**, 276; *Chem. Abs.*, 1934, **28**, 2321; *Brit. Chem. Abs.* **A**, 1934, 276. *Cf.* also V. E. Levine and E. Richman, *J. Biol. Chem.*, 1933, **101**, 373; *Brit. Chem. Abs.* **A**, 1933, 987; *Chem. Abs.*, 1933, **27**, 3975. *Biochem J.*, 1933, **27**, 2051; *Chem. Abs.*, 1934, **28**, 3392; *Brit. Chem. Abs.* **A**, 1934, 199.

[15] J. Varga and I. Makray (*Brennstoff-Chem.*, 1932, **13**, 248; *Brit. Chem. Abs.* **B**, 1932, 826; *Chem. Abs.*, 1932, **26**, 5196) have observed this also in studying the action of sulphuric acid on a benzine from cracked brown-coal tar.

[16] See for example N. Dănăilă, Th. Ionescu and R. Verona, *Bul. Chim. Soc. Române Chim.*, 1932, **35**, 107; *Chem. Abs.*, 1934, **28**, 3569; *J. Inst. Pet. Tech.*, 1934, **20**, 242A. *Cf.* also A. F. Dobryanskii and N. D. Gadaskina, *Materials on Cracking and Chemical Treatment of Products Obtained, Khimteoret, (Leningrad)*, 1935, **2**, 223; *Chem. Abs.*, 1935, **29**, 6032; *Brit. Chem. Abs.* **B**, 1936, 631.

Milas and McAlevy[17] observed that furoperacid[18] may be used for the estimation of unsaturated hydrocarbons but that quantitative results were not obtained in all cases. This is also the case with other peracids, such as perbenzoic and percamphoric acids.[19]

Halogenation of unsaturated linkages has been proposed also. For example, the slow liberation of bromine (in the presence of olefinic hydrocarbons) from an aqueous solution of potassium bromate and bromide by sulphuric acid is said to be a useful method. Under these conditions there is little tendency for substitution of hydrogen (in the hydrocarbon) by the halogen to occur. This procedure, which was developed by Francis,[20] has been modified somewhat by Mulliken and Wakeman.[21] The amount of bromide-bromate solution to be added is 2 cc. less than the amount necessary for the alkene which would boil 25°C. higher than the sample under investigation. The procedure is given:

The calculated amount of standardized bromide-bromate solution is run into a 118 cc. (4-oz.) glass-stoppered bottle, 0.5 cc. of hydrocarbon is then added, and finally 15 cc. of 10 per cent sulphuric acid. The bottle is stoppered quickly and shaken well until the bromine color vanishes and does not reappear when agitation is temporarily stopped. If, instead of disappearing, a visible bromine color still remains after 2 minutes' shaking, 5 cc. of 15 per cent potassium iodide are added and the liberated iodine is titrated with $0.2N$ thiosulphate solution. If, on the other hand, the color disappears, more bromide-bromate solution is added, 1 cc. at a time, until a visible yellow color finally persists after 2 minutes of shaking. Titration is then completed.

This procedure was found to be suitable for determination of the degree of unsaturation in alkenes, cycloalkenes and alkadienes, but not for alkynes and only doubtfully in terpenes. Titration of cyclopentadiene by the bromide-bromate method gives inaccurate results, largely due to formation of a peroxide of the hydrocarbon.[22]

Other methods by which halogenation may be effected involve the use of iodine, bromine, iodine chloride, or a solution of iodine bromide in glacial acetic acid.[23] Some difficulty is frequently experienced in using these reagents with dark-colored petroleum oil because of masking of the color of the iodine or bromine.

Hugel and Krassilchik[24] have applied the thiocyanogen number (which has found some application in the study of fats and oils) to the estimation of the unsaturation of hydrocarbons. The reagent in the present instance consists of a solu-

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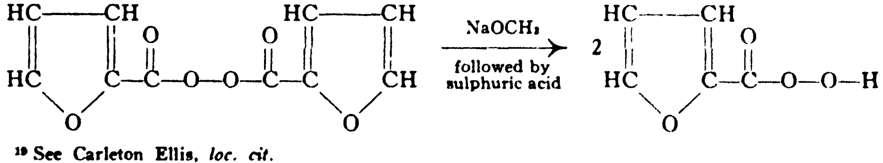
[17] N. A. Milas and A. McAlevy, *J.A.C.S.*, 1934, **56**, 1219; *J. Inst. Pet. Tech.*, 1934, **20**, 407A; *Brit. Chem. Abs.* **A**, 1934, 778; *Chem. Abs.*, 1934, **28**, 4413.

[18] Furoperacid is prepared by treating difuroyl peroxide (from furoyl chloride and sodium peroxide) with sodium methoxide in anhydrous ether.



[19] See Carleton Ellis, *loc. cit.*

[20] A. W. Francis, *Ind. Eng. Chem.*, 1926, **18**, 821, 1095; *Chem. Abs.*, 1927, **21**, 645; *Brit. Chem. Abs.* **B**, 1926, 811.

[21] S. P. Mulliken and R. L. Wakeman, *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 59; *Chem. Abs.*, 1935, **29**, 1362; *Brit. Chem. Abs.* **A**, 1935, 324; *J. Inst. Pet. Tech.*, 1935, **21**, 126A.

[22] G. R. Schultze, *J.A.C.S.*, 1934, **56**, 1552; *Brit. Chem. Abs.* **A**, 1934, 995; *Chem. Abs.*, 1934, **28**, 5047.

[23] E. Rossmann, *Angew. Chem.*, 1935, **48**, 223; *Chem. Abs.*, 1935, **29**, 4611; *Brit. Chem. Abs.* **A**, 1935, 728. Volmar and Wagner. *Bull. soc. chim.*, 1935, (5) **2**, 826; *Chem. Abs.*, 1935, **29**, 5815; *Brit. Chem. Abs.* **A**, 1935, 843. E. E. Casimer and M. Dimitriu, *Petroleum Z.*, 1935, **31**, No. 33, 1; *Brit. Chem. Abs.* **B**, 1935, 890; *J. Inst. Pet. Tech.*, 1935, **21**, 369A; *Chem. Abs.*, 1936, **30**, 845. E. Galle and R. Klatt, *Brennstoff-Chem.*, 1933, **14**, 321; *Chem. Abs.*, 1933, **27**, 5933; *Brit. Chem. Abs.* **B**, 1933, 901.

[24] G. Hugel and A. Krassilchik, *9th Cong. Chim. Ind., Barcelona*, **1929**; *J. Inst. Pet. Tech.*, 1929, **15**, 744; *Chim. et ind. Special No.*, 203, 1930; *Chem. Abs.*, 1930, **24**, 5714.

tion of thiocyanogen in an organic solvent such as acetic acid. This may be prepared either from lead thiocyanate and bromine or by the addition of bromine to a solution of sodium thiocyanate in glacial acetic acid.[25] Thiocyanate numbers have been used in the study of the composition of cracked gasoline. The results indicated that there was some difference in the reaction between an olefin and thiocyanogen from that between an olefin and mercuric acetate.[26]

ESTIMATION OF UNSATURATION BY HYDROGENATION

Procedures for the estimation of unsaturation by addition of halogens or thiocyanogen have the serious disadvantage that combination is only quantitative in certain cases, such as with normal alkenes. Some diolefins, e.g., isoprene and 2,4-dimethylpentadiene-1,3, give bromine numbers which are approximately one-half of the theoretical value. De Kok, Waterman and van Westen[27] have described a method of hydrogenation of organic substances by which it is possible to determine the degree of unsaturation readily. Their procedure is to bring a weighed amount of substance and a measured volume of hydrogen in intimate contact with an oxygen-free palladium- or platinum-on-asbestos catalyst at about 200°C. After reaction, the excess hydrogen is pumped into a gas burette where the volume is measured. From the amount of gas thus united, the unsaturation of the compound may be calculated. Some of the results obtained by the hydrogenation method are compared with the corresponding values obtained by the bromine method of McIlhiney[28] as shown in Table 212.

TABLE 212.—*Hydrogenation of Unsaturated Compounds.*

Compound	Hydrogen Value. Per Cent of Theory	Bromine Value. Per Cent of Theory
Olefins		
Amylene	100.8	100.4
Hexene-1	101.1	99.9
Heptene-1	100.3	98.2
Octene-1	100.6	100.3
Decene	101.4	100.7
Hexadecene	99.6	99.9
Diolefins		
Isoprene	99.7	50.0
2,4-Dimethylpentadiene-1,3	101.4	42.8–48.6
2,5-Dimethylheptadiene	101.0	65.5–67.4
Cyclic Compounds		
Cyclohexene	100.3	99.8
α-Pinene	99.9	>100.
Styrene (Pd catalyst)	100.8	100.3
Styrene (Pt catalyst)	100.3	100.3

[25] H. P. Kaufmann and W. Oehring, *Ber.*, 1926, **59**, 187; *Chem. Abs.*, 1926, **20**, 1603; *Brit. Chem. Abs.* **A**, 1926, 392. H. P. Kaufmann, *Arch. Pharm.*, 1925, **263**, 675; *Brit. Chem. Abs.* **B**, 1926, 165; *Chem. Abs.*, 1926, **20**, 882. *Z. Untersuch. Lebensm.*, 1926, **51**, 15; *Chem. Abs.*, 1926, **20**, 2256; *Brit. Chem. Abs.* **B**, 1926, 447. *Ber.*, 1926, **59**, 1390; *Chem. Abs.*, 1926, **20**, 2989; *Brit. Chem. Abs.* **B**, 1926, 758. British P. 257,619, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1927, **21**, 3057; *Brit. Chem. Abs.* **B**, 1928, 516. German P. 484,360, 1925; *Chem. Abs.*, 1930, **24**, 1119. *Allgem. Öl-Fettztg.*, 1930, **27**, 39; *Chem. Abs.*, 1930, **24**, 2000. *Chem. Umschau Fette, Oele Wachse Harze*, 1930, **37**, 113; *Chem. Abs.*, 1930, **24**, 4177. H. P. Kaufmann and R. Walther, *Allgem. Öl-Fettztg.*, 1930, **27**, 4; *Chem. Abs.*, 1930, **24**, 1998. H. P. Kaufmann and H. Grosse-Oetringhaus, *Ber.*, 1937, **70**, 911.

[26] P. S. Panyutin and N. V. Milovidova, *Collection Repts. Motor Fuel Research, U.S.S.R. Trans. Sci. Automobile-Tractor Inst. Issue*, 1931, **21**, 33; *Chem. Abs.*, 1932, **26**, 4457; *Brit. Chem. Abs.* **B**, 1932, 969.

[27] W. J. C. de Kok, H. I. Waterman and H. A. van Westen, *J.S.C.I.*, 1936, **55**, 225T; *Chem. Abs.*, 1936, **30**, 7929.

[28] A method which permits the determination of the halogen which takes part in substitution as well as addition reactions. See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

When styrene was hydrogenated using a palladium catalyst, only the side chain was affected; however, in the presence of a platinum catalyst the reaction resulted in the formation of ethylcyclohexane.[29]

ESTIMATION OF AROMATIC HYDROCARBONS IN PETROLEUM DISTILLATES

Among the hydrocarbons which occur in petroleum, aromatics are of particular interest because of their high octane rating (Chapter 44), and many procedures have been suggested for their determination.[30] One depends upon the sulphonation of aromatics by the action of 98 to 100 per cent sulphuric acid.[31] In most cases it has been found that benzene is somewhat difficult to remove completely and quantitatively, although its homologues are more readily sulphonated.[32] Virobyantz[33] has proposed that a portion of the aromatic compounds, which are removed by agitating a distillate with 97 to 99 per cent sulphuric acid for five hours, be recovered by diluting the separated acid solution with an equal volume of water and distilling with steam superheated to 200 or 210°C. Between 50 and 90 per cent of the compounds are said to be regained by this method.

In most procedures involving the use of sulphuric acid, any olefins present in the sample under investigation are either eliminated by treatment with a more dilute acid than that necessary to sulphonate aromatics, or are removed simultaneously with aromatics. However, Vlugter[34] has suggested that the alkenes be hydrogenated selectively in the presence of a specially prepared molybdenum catalyst at 300°C. The aromatics can then be determined in the usual way with sulphuric acid.

Nitration, using nitric and sulphuric acids or nitric acid alone, has been recommended as a method for the estimation of aromatic hydrocarbons. Olefins, when present, are first removed by shaking the gasoline with 85 per cent sulphuric acid. Twenty cc. of the olefin-free sample are then agitated with a nitrating mixture in a 200 cc. round-bottomed flask provided with a graduated neck. Care is taken to insure against excessive rise in temperature. The loss in volume gives the aromatic content of the gasoline. If this is greater than 20 per cent, the original gasoline must be diluted with an aromatic-free distillate before carrying out the determination.[35]

Dobryanskiĭ and Tikhonov-Dubrovskiĭ[36] have outlined a procedure which depends upon reaction with trinitrophenol. Naphthalene has been determined by a somewhat similar procedure.[37] A 0.7 per cent solution of picric acid is placed in each of three wash bottles connected in series. The sample to be tested is placed in the first bottle which is cooled by cold water. The other bottles are maintained at 0°C. by ice baths. A slow stream of air passes through the apparatus until the gasoline has been completely removed from all three containers. The naphthalene, which forms a molecular compound with picric acid, is then determined in the usual way.[38]

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[29] Using a nickel catalyst, H. I. Waterman and C. van Vlodrop (*Rec. trav. chim.*, 1936, **55**, 401) have shown that peanut oil and naphthalene are hydrogenated simultaneously at atmospheric pressure and 180°C.

[30] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. See also *Österr. Petroleum Inst. Publ.*, 1935; *Brit. Chem. Abs.* **B**, 1936, 1077.

[31] See, for example, P. S. Maslov and E. I. Kozuireva, *Groznenskiĭ Neftyanik*, 1934, **4**, No. 5, 26; *Brit. Chem. Abs.* **B**, 1935, 1030; *Chem. Abs.*, 1935, **29**, 2716. *Cf.* H. Barsch, *Z. anal. Chem.*, 1935, **100**, 280; *Chem. Abs.*, 1935, **29**, 3200; *Brit. Chem. Abs.* **A**, 1935, 639.

[32] R. Verona, *Bull. Chim. Soc. Române Chim.*, 1934, **37**, 221; *Chem. Abs.*, 1935, **29**, 6392; *Brit. Chem. Abs.* **B**, 1935, 710. See also S. S. Nametkin and E. A. Robinzon, *Neft. Khoz.*, 1933, **24**, 184, 230; *Chem. Abs.*, 1934, **28**, 301; *Brit. Chem. Abs.* **B**, 1934, 308. S. S. Nametkin, *U.S.S.R. Sci.-Tech. Dept. Supreme Council of National Economy*, No. 372, *Trans. Institute Petroleum Research*, **1930**, No. 8; *Chem. Zentr.*, 1931, **1**, 383. E. Wendehorst and E. Knoche, *Angew. Chem.*, 1934, **47**, 43; *Chem. Abs.*, 1934, **28**, 2172; *Brit. Chem. Abs.* **B**, 1934, 179.

[33] R. A. Virobyantz, *Neft. Khoz.*, 1933, **25**, 160; *Brit. Chem. Abs.* **B**, 1934, 820; *Chem. Abs.*, 1934, **28**, 3227.

[34] S. C. Vlugter, *J. Inst. Pet. Tech.*, 1935, **21**, 36; *Chem. Abs.*, 1935, **29**, 2717; *Brit. Chem. Abs.* **B**, 1935, 342.

[35] F. Lang, *Petroleum Z.*, 1936, **32**, No. 8, 1; *Chem. Abs.*, 1936, **30**, 3989; *Brit. Chem. Abs.* **B**, 1936, 435. *Cf.* H. H. Weber and F. Hauck, *Chem.-Ztg.*, 1933, **57**, 836, 915; *Chem. Abs.*, 1934, **28**, 727; *Brit. Chem. Abs.* **B**, 1934, 85. H. H. Schrenk, S. J. Pearce and W. P. Yant, *U. S. Bureau of Mines Rept. of Investigations*, No. **3287**, 1935; *Chem. Abs.*, 1935, **29**, 7869. For a color reaction obtained by nitrating benzene to *m*-dinitrobenzene and treating the latter with butanone and sodium hydroxide, see *Fuel*, 1936, **15** (1), 4; *J. Inst. Pet. Tech.*, 1936, **22**, 48A.

[36] A. F. Dobryanskiĭ and N. T. Tikhonov-Dubrovskiĭ, *Azer. Neft. Khoz.*, **1935**, No. 5, 84; *J. Inst. Pet. Tech.*, 1936, **22**, 301A; *Chem. Abs.*, 1936, **30**, 3989.

Under some conditions, oxidation of side-chains on aromatic hydrocarbons may be used in the analysis of the latter.[39] Reaction may be effected either with chromic acid or a permanganate. Since the oxidation of ortho-substituted dialkyl benzenes with chromic acid may result in breaking the ring structure, it is usually better to substitute this agent by alkaline permanganate.[40]

Aromatic and olefin hydrocarbons may be separated from naphthenes and paraffins by filtration through silica gel.[41] The extent to which the removal proceeds depends largely upon the composition of the sample, as well as the precise compounds involved. It has been noted that considerable loss results in attempting to recover the adsorbed hydrocarbons by distillation from the adsorbing medium.

Estimation of Paraffin Wax. The paraffinic hydrocarbons, together with the cycloparaffins or naphthenes, form the major constituents of petroleum oils. For that reason, determination of these hydrocarbons, except in certain isolated cases, is not very common. It is, however, sometimes necessary to determine the mixture of solid hydrocarbons (often simply called "paraffin") which are dissolved in oil.[42] The sample is dissolved in a solvent, such as ether, and the paraffin precipitated by the addition of a solution consisting of equal volumes of ether and alcohol or of chloroform and cresol and cooling to —21°C. In some instances, the liquid portion (of the specimen) which boils up to about 280°C. is removed by distillation at 30 mm. pressure. Asphaltic bodies may be extracted by treating a sample of the oil in gasoline with a bleaching earth.[43] A solution of 3 parts ethyl acetate and 1 part alcohol has also been recommended for removing oil from paraffin.[44]

The waxes in an asphalt may be determined by first extracting with gasoline, and then dissolving the residue in warm pyridine. On cooling the latter solution to 0°C. the paraffin wax crystallizes out. It is filtered and washed with pyridine. It is then dissolved in benzene for further treatment with activated carbon and clay to eliminate any entrained asphalt. After the latter operation the paraffin is crystallized, washed and dried.[45]

In one method for estimation of asphalt and paraffin in a sample of crude petroleum, a 2-3 g. portion in a weighed flask is extracted with boiling acetone, leaving an asphaltic residue which is then weighed.[46] The acetone extract is cooled to —20°C. to precipitate wax, which is filtered, redissolved in hot benzene, and the latter subsequently evaporated. The wax may then be weighed.

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[37] W. Zweig and F. Kossendey, *Gas. u. Wasserfach*, 1935, **78**, 602; *Chem. Abs.*, 1935, **29**, 7041.

[38] F. W. Kuster, *Ber.*, 1894, **27**, 1101; *J.C.S.*, 1894, **66**, 333.

[39] M. S. Nemtzov and I. Shenderovich, *Khim. Tverdogo Topliva*, 1935, **6**, 729.

[40] See R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley & Sons, Inc., New York, **1935**.

[41] B. J. Mair and J. D. White, *J. Research Natl. Bur. Standards*, 1935, **15**, 51 (Paper No. **809**); *Brit. Chem. Abs.* **B**, 1935, 886; *Chem. Abs.*, 1935, **29**, 6739. H. Hofmeier and H. Meiner, *Angew. Chem.*, 1933, **46**, 229; *Chem. Abs.*, 1933, **27**, 2931; *Brit. Chem. Abs.* **B**, 1933, 497.

[42] See A. Chmelévsky, *Rev. pétrolifère*, **1932**, 982; *Chem. Zentr.*, 1932, **2**, 2574; *Chem. Abs.*, 1933, **27**, 5954.

[43] R. Heinze and A. Zwergal, *Öl u. Kohle*, 1934, **2**, 7, 154; *Chem. Abs.*, 1935, **29**, 7057; *Brit. Chem. Abs.* **B**, 1935, 391; *J. Inst. Pet. Tech.*, 1934, **20**, 242A, 449A. See also, A. Zwergal, *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 431; *Brit. Chem. Abs.* **B**, 1935, 886; *J. Inst. Pet. Tech.*, 1935, **21**, 335A; *Chem. Abs.*, 1935, **29**, 8301.

[44] A. M. Ravikovich and V. N. Shile, *J. Applied Chem.* (*U.S.S.R.*), 1935, **8**, 172; *Chem. Abs.*, 1935, **29**, 7058; *Brit. Chem. Abs.* **B**, 1935, 710; *J. Inst. Pet. Tech.*, 1936, **22**, 92A.

[45] V. Parini, *Neft*, 1933, **4**, No. 5, 18; *Brit. Chem. Abs.* **B**, 1935, 1028; *Chem. Abs.*, 1935, **29**, 2726.

[46] I. L. Blum, *Bul. Chim., Soc. Române Chim.*, 1935-36, **38**, 155; *Chem. Abs.*, 1937, **31**, 1989; *Brit. Chem. Abs.* **B**, 1937, 107.

TESTS FOR SULPHUR AND SULPHUR COMPOUNDS

Practically all types of sulphur compounds have been found in crude petroleum or its distillates, though the proportions of such derivatives vary in oils from different sources. Their presence is considered undesirable because of their unpleasant odor (particularly mercaptans or thiols) and also because on oxidation they give rise to substances held to be corrosive (largely sulphur dioxide). The proportion of sulphur in motor fuels in amounts greater than 0.10 per cent is thought by some to cause excessive attack on the motor because of the formation of sulphur dioxide during combustion.[47] The usual tests for sulphur and its compounds in petroleum distinguish between elemental sulphur, hydrogen sulphide, sulphur dioxide and mercaptans, all of which are considered to be particularly nocuous, and the other sulphur-containing compounds which are classed as "residual" sulphur and may be comparatively inoffensive. Sentzov and Chadaeva[48] have noted that elemental sulphur is the most corrosive form of this element. Hydrogen sulphide and mercaptans are also said to be corrosive, although to a lesser extent, but sulphides, disulphides and thiophenes may be considered to be innocuous.

Elemental Sulphur. One procedure commonly employed consists in keeping a copper strip in contact with the petroleum distillate 3 hours at a temperature of 122°F.[49] A discoloration of the strip indicates the presence of elemental sulphur. Alexandrov[50] recommends a temperature of 150°C. and a period of 15 minutes. Operations may be carried out under a reflux condenser. It has been suggested that the copper strip be cleaned by treatment with 5 per cent aqueous ammonia and then oxalic acid.[51]

Another test used in some cases depends upon the reaction of mercury with sulphur. A small proportion of hydrochloric acid is also added to coagulate the sulphide formed. The sulphide is oxidized during digestion with hydrochloric acid by the addition of a small amount of potassium perchlorate. Barium sulphate is then precipitated and weighed. This method has been used by Gabriel'yantz and Artem'eva[52] for the determination of free sulphur in the distillates from Grozny asphalt-base and Baku crude oils. A modification developed by Pieters and his co-workers[53] consists in decomposing the mercuric sulphide with hydrochloric acid and absorbing the liberated hydrogen sulphide in aqueous cadmium acetate. The sulphur was then determined by iodimetry. The results were said to be identical with those obtained using sodium hydroxide and hydrogen peroxide for oxidation of the sulphide.

A rapid determination of sulphur, said to be applicable to the control of doctor sweetening processes, has been developed.[54] In the determination a known quantity of butyl mercaptan in naphtha is added to the gasoline under analysis. The mixture is then agitated with doctor solution until complete reaction of the sulphur and the added mercaptan has occurred. Since the excess mercaptan is now present as lead mercaptide, it is restored to the original mercaptan by dilute sulphuric acid. The gasoline is then washed with acidified cadmium chloride solution (to remove hydrogen sulphide) and titrated with silver nitrate solution[55] to determine the excess mercaptan. The used mercaptan, obtained by difference, permits a calculation of the free sulphur content of the original gasoline.

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[47] The chemistry of the sulphur compounds in petroleum is discussed in Chapter 19. See also, E. Dittrich, *Brennstoff-Chem.*, 1933, **14**, 383; *J. Inst. Pet. Tech.*, 1934, **20**, 78A.

[48] P. A. Sentzov and L. F. Chadaeva, *Groznenskiĭ Neftyanik*, 1934, **4** (6-7), 37-40; *Chem. Abs.*, 1935, **29**, 2719; *Brit. Chem. Abs.* **B**, 1935, 1031.

[49] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[50] L. A. Alexandrov, *Groznenskiĭ Neftyanik*, 1934, **4** (5), 52; *Chem. Abs.*, 1935, **29**, 2719.

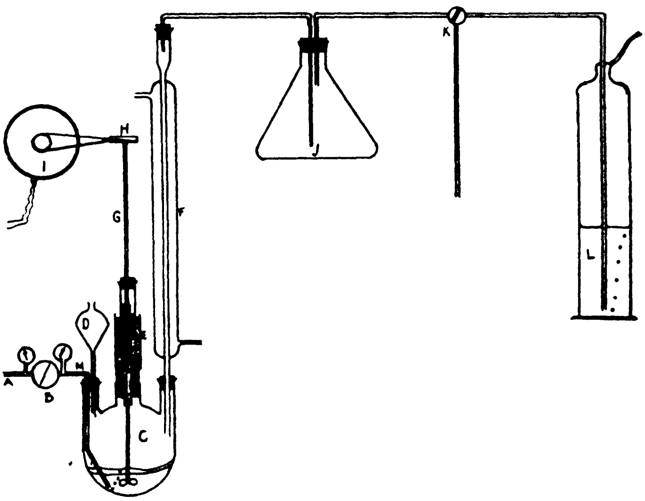
[51] E. G. Ivanovna, *Neft*, 1936, **7** (6), 21; *Chem. Abs.*, 1936, **30**, 6178; *J. Inst. Pet. Tech.*, 1936, **22**, 438A.

[52] S. M. Gabriel'yantz and O. A. Artem'eva, *Groznenskiĭ Neftyanik*, 1934, **4** (8), 41; *Brit. Chem. Abs.* **B**, 1935, 1029; *Chem. Abs.*, 1935, **29**, 2725.

[53] H. A. J. Pieters, J. R. van Iterson and S. J. H. Spronck, *Chem. Weekblad*, 1933, **30**, 756; *Brit. Chem. Abs.* **B**, 1934, 132; *Chem. Abs.*, 1934, **28**, 1303.

[54] C. Wirth III and J. R. Strong, *Ind. Eng. Chem.*, *Anal. Ed.*, 1936, **8**, 344; *Brit. Chem. Abs.* **B**, 1936, 1138; *Chem. Abs.*, 1936, **30**, 7828; *J. Inst. Pet. Tech.*, 1936, **22**, 498A.

In another method the free sulphur is converted to mercaptans by the action of hydrogen, and determined as mercaptans.[56] The apparatus (Fig. 288) consists of a flask for converting the sulphur, a condenser, gasoline trap and gas washing bottle containing ammoniacal cadmium chloride. The distillate under analysis is placed, together with reduced iron, in the reaction flask, and hydrochloric acid slowly added. The liberated hydrogen reacts with sulphur to form mercaptans. The latter are conducted to the gas bottle, where the hydrosulphides are determined iodimetrically.



A. Inert gas supply
B. Reducing valve
C. 3-Neck liter flask
D. Dropping funnel. 50 cc.
E. Mercury seal
F. Condenser
G. Stirrer
H. Pulley
I. Variable speed motor
J. Trap (100 cc. Erlenmeyer)
K. Three-way stopcock
L. Gas washing bottle, filled with ammoniacal cadmium chloride solution, for absorbing hydrogen sulphide
M. Gas inlet tube

Courtesy Industrial and Engineering Chemistry

FIG. 288.—Sketch of Apparatus for Determination of Free Sulphur in Petroleum Distillates. (S. Comay)

Mercaptans. The presence of these compounds in gasoline or kerosene is indicated by the doctor test (using sodium plumbite). This is said to detect methyl, butyl and heptyl mercaptans in concentrations equivalent to 0.002, 0.0002 and 0.00009 per cent of sulphur, respectively.[57] Berger[58] determines the mercaptan content of a gasoline by titration with an aqueous solution of a copper salt. This reagent is made by dissolving 3.91 g. of copper sulphate in 300 cc. of water, chilling, precipitating completely with cold sodium hydroxide (5°Bé. gravity), and finally dissolving the precipitated cupric hydroxide by the addition of cold ammonium hydroxide. The solution is then diluted to 1 liter. It must be kept ice-cold throughout the preparation. Titration is carried out by adding 1 cc. portions of the test solution to 100 cc. of sour gasoline (free from hydrogen sulphide) in a 250 cc. separatory funnel until the blue color of the aqueous layer no longer disappears.

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[55] See Carleton Ellis, "The Chemistry of Petroleum Derivatives, "The Chemical Catalog Co., Inc., New York, 1934.

[56] S. Comay, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 460.

[57] G. A. Boyd, *Oil Gas J.*, 1933, **32** (8), 16, 31; *Chem. Abs.*, 1933, **27**, 5525.

[58] C. W. Berger, *Refiner*, 1935, **14**, 470; *Chem. Abs.*, 1935, **29**, 8303.

A somewhat different method for the determination of thiols consists in oxidizing them with cupric chloride and estimating the cuprous chloride formed by means of potassium permanganate.[59] Bond[60] has described the titration of mercaptans in gasoline in which a standard solution of copper oleate is used. The solution is made up in kerosene and contains about 4 g. of copper per liter. The end point is a pale green color, which is said to be visible even in the presence of considerable precipitate. The method was found to precipitate mercaptans and hydrogen sulphide, but not to be influenced by the presence of carbon disulphide, organic disulphides or octene. Peroxides, which might develop in the copper oleate solution through oxidation, were injurious to the accuracy of the results. A comparison of this test with the silver nitrate method of Borgstrom and Reid[61] and with an iodimetric method showed that the copper oleate titration gave fairly accurate results.

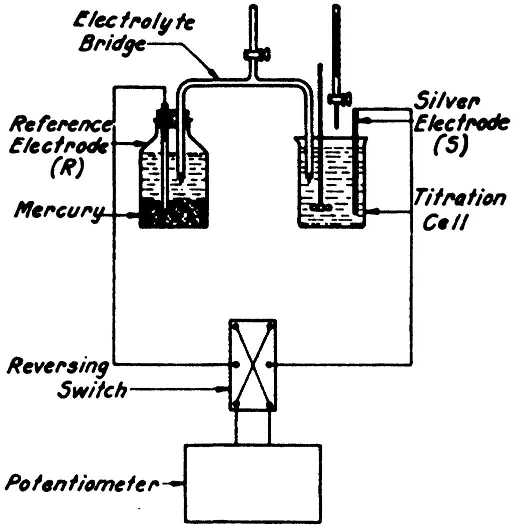

FIG. 289. Diagram of Apparatus for Potentiometric Determination of Mercaptans. (M. W. Tamele and L. B. Ryland)

Courtesy Industrial and Engineering Chemistry

The silver nitrate method, which is similar to Volhard's well-known procedure for the determination of soluble halides,[62] has been modified by different workers. Thus, Malisoff and Anding[63] have recommended the addition of methanol to the solution to minimize the tendency to form emulsions. This was also found to shorten the time required for shaking and washing the precipitate. A source of error has always been the silver adsorbed and occluded by the precipitated silver mercaptide. Malisoff and Anding decreased this somewhat, but the potentiometric method described by Tamele and Ryland[64] is said to give even better results. The procedure is briefly: Add the sample to 50 cc. of approximately 0.1*N* sodium acetate in 96 per cent ethyl alcohol. This solution is part of the silver half-cell of the cell:

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[59] W. A. Schulze and L. V. Chaney, *Nat. Pet. News*, 1933, 25 (34), 37; *Chem. Abs.*, 1933, 27, 5952.

[60] G. R. Bond, Jr., *Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 257; *Brit. Chem. Abs.* B, 1933, 773, *Chem. Abs.*, 1933, 27, 4192.

[61] P. Borgstrom and E. E. Reid, *Ind. Eng. Chem., Anal. Ed.*, 1929, 1, 186; *Chem. Abs.*, 1929, 23, 5439; *Brit. Chem. Abs.* B, 1929, 1004.

[62] J. Volhard, *J. prakt. Chem.*, 1874, 9 (2), 217; *Chem. Zentr.*, 1874, I, 407; *J.C.S.*, 1874, 27, 919. See also, M. A. Rosanoff and A. E. Hill, *J.A.C.S.*, 1907, 29, 269; *Chem. Abs.*, 1907, 1, 1367; *J.C.S.*, 1907, 92, 503.

[63] W. M. Malisoff and C. E. Anding, Jr., *Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 86; *Brit. Chem Abs.* B, 1935, 484; *Chem. Abs.*, 1935, 29, 3628.

−Ag	0.1*N* sodium acetate in alcohol	0.1*N* sodium acetate in alcohol	+Hg

The apparatus recommended is shown in Fig. 289. The e.m.f. of the cell before addition of the sample is approximately —0.070 volts (silver being the negative electrode). If mercaptans are in the liquid under investigation, then the potential of the silver electrode becomes about —0.380 volts. A standard solution (about 0.01*N*) of silver nitrate in 2-propanol is added slowly and the changes in e.m.f. recorded. A sudden drop in the negative potential occurs at the end point. When the e.m.f. is plotted against the volume of standard solution used, a curve, such as that shown in Fig. 290, is obtained. Tamele and Ryland observed that the accuracy of their procedure was not greatly affected by the presence of substances which react with silver nitrate, such as chlorides, because of the extreme insolubility of the silver mercaptides. Peroxides, which were found to vitiate the results of the copper oleate titration, did not influence the potentiometric determination to any appreciable extent. It was necessary, however, to remove elemental sulphur and hydrogen sulphide from the sample.

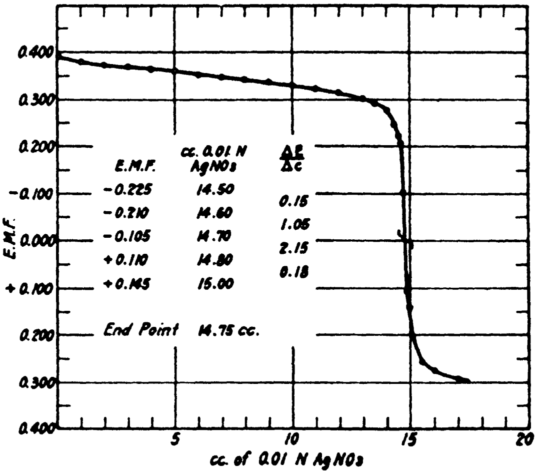

FIG. 290.
Representative Titration Curve for *n*-Butyl Mercaptan in Kerosene. (M. W. Tamele and L. B. Ryland)

Courtesy Industrial and Engineering Chemistry

The presence of the alkyl thiols and thioethers may be shown by the use of the sodium nitroprusside test.[65] This test is ordinarily carried out in the presence of sodium hydroxide. Alkyl sulphides, such as methyl, ethyl, propyl, butyl and amyl sulphides, are said to give violet colorations. Thiophenol gives a reaction only when aqueous ammonia is employed as the alkali. Aryl and aralkyl sulphides do not respond to this test.

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[64] M. W. Tamele and L. B. Ryland, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 16; *Brit. Chem. Abs.* **B**, 1936, 307; *Chem. Abs.*, 1936, **30**, 1329; *J. Inst. Pet. Tech.*, 1936, **22**, 19A.

[65] L. Hermejo and J. J. Herrera, *Anales soc. españ. fis. quim.*, 1933, **31**, 48; *Brit. Chem. Abs.* **A**, 1933, 964; *Chem. Abs.*, 1933, **27**, 1593. J. J. Herrera and L. Hermejo, *ibid.*, 1933, **31**, 267; *Brit. Chem. Abs. B*, 1933, 819. T. Pavolini (*Boll. chim.-farm.*, 1930, **69**, 713, 719; *Chem. Abs.*, 1931, **25**, 2933; *Brit. Chem. Abs.* **A**, 1930, 1605) has outlined the many color reactions which are given by sodium nitroprusside ($Na_2Fe(CN)_5NO$).

Total Sulphur. Determination of the total sulphur content of a petroleum fraction is effected in either of two ways. For the analysis of fairly volatile fractions, such as kerosene and petroleum naphtha, the lamp method[66] is widely used. An oxygen-bomb method[67] has been adopted for non-volatile fractions.

The apparatus for sulphur analysis by the lamp method consists of a 25 to 35 ml. Erlenmeyer flask fitted with a wick, chimney, absorbing bulbs and spray trap[68] as shown in Fig. 291. The procedure is to place a sample of gasoline in the small flask. The wick is cut to the desired length and the lamp and contents weighed. The sample is burned and the vapors drawn by a slight suction through the absorbing bulbs which contain 10 cc. of standard sodium carbonate (3.306 g. per liter)

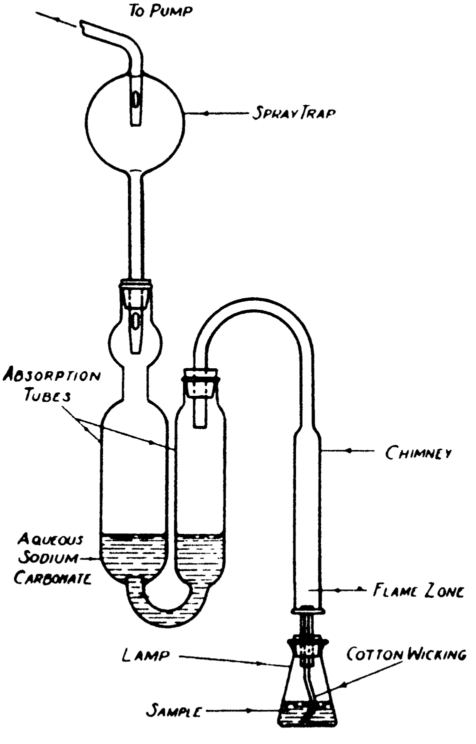

FIG. 291.
Sketch of Apparatus for Sulphur Determination by A.S.T.M. Method.

For details of procedure and specifications of apparatus see A.S.T.M. Method D90-34T; "A.S.T.M. Tentative Standards," American Society for Testing Materials, Philadelphia, **1935**, 746.

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[66] A.S.T.M. D 90-34T; A.S.A. No. Z11.38-1935; A.S.T.M. Tentative Standards, American Society for Testing Materials, Philadelphia, 1935.

[67] A.S.T.M. D 129-33; A.S.A. No. Z11.13-1933; A.P.I. No. 516-33; A.S.T.M. Standards, American Society for Testing Materials, Philadelphia, 1933.

[68] Some changes in the design of the lamp used in this determination have been suggested by: G. Edgar and G. Calingaert, *Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 104; *Chem. Abs.*, 1930, **24**, 1732; *Brit. Chem. Abs.* **B**, 1930, 402. R. H. Espach and O. C. Blade, *Bur. Mines Tech. Paper*, **1931**, 513; *Chem. Abs.*, 1932, **26**, 1106. E. R. Gillis, *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 421; *Brit. Chem. Abs.* **B**, 1934, 51; *Chem. Abs.*, 1934, **28**, 885. H. O. Ervin, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 225; *Brit. Chem. Abs.* **B**, 1934, 613; *J. Inst. Pet. Tech.*, 1934, **20**, 450A; *Chem. Abs.*, 1934, **28**, 3689. R. M. Lilly, *Refiner*, 1934, **13** (5), 177; *J. Inst. Pet. Tech.*, 1934, **20**, 406A; *Brit. Chem. Abs.* **B**, 1934, 1045; *Chem. Abs.*, 1934, **28**, 5641. See also, F. Esling, *J. Inst. Pet. Tech.*, 1921, **7**, 83; *J.S.C.I.*, 1921, **40**, 500A; *Chem. Age (London)*, 1920, **3**, 684; *Chem. Abs.*, 1921, **15**, 812. *J. Inst. Pet. Tech.*, 1934, **20**, 1051; *Brit. Chem.* Abs. **B**, 1935, 179; *J. Inst. Pet. Tech.*, 1935, **21**, 15A; *Chem. Abs.*, 1935, **29**, 1686.

solution. The time required for burning is from 1 to 1.5 hours, and the oil should be consumed at the rate of about 2 to 2.5 g. per hour. At the end of this time the portion of the unreacted sodium carbonate is determined by titration with dilute hydrochloric acid (2.275 g. per liter). A blank is run at the same time as the sample but using sulphur-free alcohol as the fuel. The results are calculated according to the formula:

$$\text{Per cent sulphur} = \frac{(\text{ml. HCl for blank}) - (\text{ml. HCl for sample})}{(\text{Grams of oil burned}) \times 10}$$

Many modifications of the lamp method have been proposed by various investigators for improving different features. For example, Heinze and Schmeling[69] suggested using a spiral glass coil for the absorption of products of combustion. Their apparatus is said to remove sulphur dioxide quantitatively from a gas stream flowing at the rate of 3 liters per minute. Chernov and Sobolev[70] recommended admitting oxygen with air (after purifying the latter) during burning of the sample. Heusler[71] found that a solution of potassium permanganate could be used for the absorption of oxides of sulphur which were afterwards estimated as sulphates. According to Engler,[72] a solution of bromine in potassium hydroxide or carbonate may be substituted for potassium permanganate. Schulz[73] absorbed the sulphur oxides in hydrogen peroxide and titrated the resulting sulphuric acid. A similar method has been used in the determination of sulphur in benzene.[74] Another absorbing agent, employed by Orlov and Broun,[75] consists of a solution of potassium dichromate and hydrochloric acid.

The oxygen-bomb method for the determination of sulphur in petroleum fractions heavier than illuminating oils consists essentially in burning the sample in an atmosphere of oxygen and precipitating the sulphuric acid formed, as barium sulphate.[76] The procedure is: Place 20 cc. of water in the bottom of the bomb. The sample (from 0.6 to 0.8 g.) of oil is placed in the weighed oil cup, and the latter put in the bomb. The ignition mechanism (an electrically heated wire) is arranged and the bomb closed. Oxygen is admitted under pressure of from 25 to 40 atmospheres. The bomb is put in a pail of water with the ignition leads attached and the sample ignited. The bomb is allowed to stand for 10 minutes before the internal pressure is released, after which it is washed out and the sulphate precipitated from the washings in the usual way with barium chloride. The weighed amount of barium sulphate, after ignition, is used to calculate the results:

$$\text{Percentage of sulphur} = \frac{\text{Grams of } BaSO_4 \times 13.734}{\text{Grams of oil used}}$$

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[69] R. Heinze and F. Schmeling *Öl u. Kohle*, 1934, **2**, 61; *Chem. Zentr.*, 1934, **2**, 1403; *Chem. Abs.*, 1935, **29**, 6475; *J. Inst Pet. Tech.*, 1934, **20**, 303A. *Cf.* French P. 800,930, 1936, to Office central de chauffe rationnelle; *Chem Abs.*, 1937, **31**, 242.

[70] G. I. Chernov and B. N. Sobolev, *Neft. Khoz.*, 1933, **25** (9), 55; *J. Inst. Pet. Tech.*, 1934, **20**, 447A; *Chem. Abs.*, 1934, **28**, 4872; *Brit. Chem. Abs.* **B**, 1935, 86.

[71] F. Heusler, *Z. angew. Chem.*, 1895, **8** (10), 285; *J.S.C.I.*, 1895, **14**, 828. See also R. Kissling, *Chem.-Ztg.*, 1896, **20**, 199; *J.S.C.I.*, 1896, **15**, 384.

[72] C. Engler, *Chem. Ztg.*, 1896, **20**, 197; *J.S.C.I.*, 1896, **15**, 383.

[73] F. Schulz, *Petroleum Rev.*, 1913, **28**, 226; *Chem. Abs.*, 1913, **7**, 1802. *Petroleum*, 1913, **8**, 585; *J.S.C.I.*, 1913, **32**, 186.

[74] G. V. Kopelevich, A. I. Brodovich and I. R. Bekht, *Khim. Tverdogo Topliva*, 1934, **5**, 652; *Chem. Abs.*, 1935, **29**, 3140; *Brit. Chem. Abs.* **B**, 1936, 6.

[75] N. A. Orlov and A. S. Broun, *Khim. Tverdogo Topliva*, 1933, **4**, 380; *Brit. Chem. Abs.* **B**, 1935, 54; *Chem. Abs.*, 1934, **28**, 6289. *For. Petr. Techn.*, 1934, **2**, 302; *J. Inst. Pet. Tech.*, 1935, **21**, 125A.

[76] R. C. Griffin (*Ind. Eng. Chem., Anal. Ed.*, 1929, **1**, 167; *Chem. Abs.*, 1929, **23**, 4382; *Brit. Chem. Abs.* **B**, 1929, 768) has reported that the oxidation of sulphur compounds in a bomb converts part of them to sulphonic acids which are not precipitated by barium chloride. However, he found that this sulphur could be recovered by refluxing the filtrate (from the barium sulphate precipitation) with hydrochloric acid. K. Weisselberg (*Petroleum Z.*, 1934, **30** (33), 1; *Chem. Abs.*, 1935, **29**, 1032) noted, on the other hand, that low results for sulphur by this method were due to the loss of sulphur dioxide. He overcame this trouble by the addition of 0.05 g. of ammonium nitrate to the bomb before ignition of the sample. E. Graefe (*Petroleum Z.*, 1934, **30** (38), 2; *Brit. Chem. Abs.* **B**, 1934, 1045) has corroborated Weisselberg's results, but he suggests that a solution of sodium peroxide be used in the bomb for absorbing the oxides of sulphur.

Gavrilenko and Rabinovich[77] modified this general method in such a way that the sulphur is determined by an iodimetric titration rather than gravimetrically. From 12 to 15 cc. of 10 per cent sodium or potassium hydroxide are put into the bomb before ignition. After the sample has been burned, the bomb is washed out with water and 7 to 8 cc. of hydrogen peroxide added to the rinsings. The solution is acidified with hydrochloric acid and then made alkaline with ammonium hydroxide. This is to precipitate iron and aluminum as phosphates (if phosphorus were present in the sample) or hydroxides. The precipitate is filtered and the filtrate acidified with hydrochloric acid and boiled for 5 minutes with a mixture of barium chloride and potassium chromate. The solution is cooled, diluted to a known volume with distilled water, mixed thoroughly and filtered. An aliquot portion (100 cc.) is treated with 3 to 4 g. of potassium iodide in water and 15 cc. of hydrochloric acid. The free iodine is titrated with $0.05N$ sodium thiosulphate (1 cc. is equivalent to 0.000535 g. sulphur). The end point is a change from blue to green (starch indicator).

Besides the two general methods mentioned above for the estimation of sulphur, there are several others which are of interest. For example, the procedure which was first used by Chabley[78] for the determination of halogen in organic compounds has been modified by Sowa, Arcadi and Nieuwland[79] so that sulphur may be determined quantitatively. Dissolve 0.1 g. of the substance in 175 cc. of liquid ammonia, and add metallic sodium until there is a permanent blue color. The resulting solution is then evaporated to 25 cc., 3 to 5 g. of ammonium chloride added and the mixture evaporated to dryness. The residue is dissolved in water, oxidized by sodium peroxide and the sulphur precipitated as barium sulphate. This method is said to be accurate and of general applicability.

Dittrich[80] proposed heating benzine with mercury, aluminum foil and hydrochloric acid. The operation liberates the sulphur as hydrogen sulphide. The latter is then absorbed and titrated with a standard solution of cupric sulphate. The Holthaus method[81] for the determination of sulphur in steel has been adapted for use in the analysis of mineral oil.[82] Combustion is carried out by passing dry oxygen over the sample (heated first to 450-650°C. and finally to 1000-1150°C.) in an electric furnace. The products of oxidation are taken up in a solution of hydrogen peroxide and titrated. A procedure by which the per cent of the various types of sulphur compounds present may be estimated has been recommended by Dubrisay.[83] The method is very similar to that used in determining the corrosiveness of a fuel. Highly polished strips of silver and copper are placed in the liquid. The extent to which these strips are discolored at the end of 48 hours is said to show the amounts of various types of sulphur compounds which are in the fuel. The absence of any effect shows that there is less than 0.001 per cent free sulphur, hydrogen sulphide or alkyl sulphides, less than 0.1 and 0.2 per cent of thiophene and carbon disulphide, respectively. Discoloration of the copper but not the silver shows the presence of free sulphur, neutral sulphides, thiophene or carbon disulphide, whereas the discoloration of silver shows the presence of mercaptans or hydrogen sulphide. Grote and Krekeler[84] have outlined an analytical procedure for the determination of sulphur and halogens in volatile, combustible substances. The method is to volatilize the sample in one portion of a glass tube and then pass it through a highly heated zone (separated from the rest of the tube by porous quartz discs) where it is burned. The products are absorbed in a specially designed absorption bulb, and the sulphate determined either titrimetrically or gravimetrically.[85]

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[77] E. S. Gavrilenko and O. B. Rabinovich, *Nauk. Zapiski Tsukrovoi Prom.*, 1933, **10** (32), 25; *Brit. Chem. Abs.* **B**, 1934, 561; *Chem. Abs.*, 1934, **28**, 2156.

[78] E. Chabley, *Ann. chim.*, 1914, **1**, 469; *J.C.S.*, 1914, **106** (I), 918A; *Chem. Abs.*, 1914, **8**, 3422. For later use of this procedure, compare F. B. Dains, T. H. Vaughan and W. M. Janney, *J.A.C.S.*, 1918, **40**, 930; *Chem. Abs.*, 1918, **12**, 1646; *J.S.C.I.*, 1918, **37**, 488A. C. W. Clifford, *J.A.C.S.*, 1919, **41**, 1051; *Chem. Abs.*, 1919, **13**, 1686; *J.S.C.I.*, 1919, **38**, 663A. F. B. Dains and R. Q. Brewster, *J.A.C.S.*, 1920, **42**, 1573; *Chem. Abs.*, 1920, **14**, 2771; *J.S.C.I.*, 1920, **39**, 642A.

[79] F. J. Sowa, V. G. Arcadi and J. A. Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 49; *Brit. Chem. Abs.* **A**, 1936, 353; *Chem. Abs.*, 1936, **30**, 1328.

[80] E. Dittrich, *Brennstoff-Chem.*, 1933, **14**, 281; *Brit. Chem. Abs.* **B**, 1933, 818; *Chem. Abs.*, 1933, **27**, 5932.

[81] C. Holthaus, *Z. angew. Chem.*, 1925, **38**, 330; *Stahl u. Eisen*, 1925, **44**, 1515; *Chem. Abs.*, 1925, **19**, 2002.

[82] I. S. Zelikov, A. N. Kotrelev and E. I. Fogelson, *Neft. Khoz.*, 1934, **26** (5), 58; *Brit. Chem. Abs.* **B**, 1935, 391; *J. Inst. Pet. Tech.*, 1935, **21**, 405A; *Chem. Abs.*, 1934, **28**, 7494.

[83] R. Dubrisay, *Chimie et industrie, April Special No.*, 401-2, 1934; *Chem. Abs.*, 1934, **28**, 5625; *Brit. Chem. Abs.* **B**, 1934, 662. *Ann. combustibles liquides*, 1933, **8**, 871; *J. Inst. Pet. Tech.*, 1933, **19**, 508A.

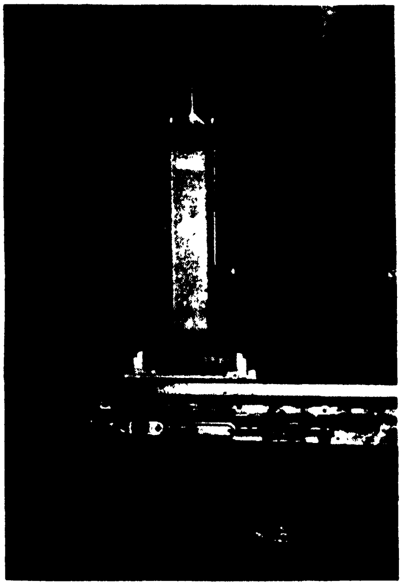

FIG. 292.
View of Apparatus for Measurement of Optical Density Color of Petroleum Oils. (S. W. Ferris and J. M. McIlvain)

Courtesy Industrial and Engineering Chemistry

COLOR TESTS

The methods which have been proposed for determining the color of various petroleum distillates may be divided into three general classes. These are: First a given thickness of the oil is matched against one of a set of standards, either glass or liquid. This is exemplified by the Lovibond Tintometer or the Union Colorimeter. In the second class are those tests in which a variable thickness of oil is matched against a standard color disk, as in the Saybolt Chromometer. The third class includes those tests in which the fraction of light absorbed by a specified thickness of oil is determined photometrically. The method described by Story and Kalichevsky[86] is an example. Koetschau[87] has recommended the use of a Zeiss-

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[84] W. Grote and H. Krekeler, *Proc. World Petr. Congr., London*, 1933, **2**, 380; *J. Inst. Pet. Tech.*, 1934, **20**, 79A; *Chem. Abs.*, 1934, **28**, 4875.

[85] W. M. Malisoff (*Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 428; *Chem. Abs.*, 1936, **30**, 48) has found that chlorine in organic compounds may be determined by much the same procedure as the standard lamp test for sulphur.

[86] B. W. Story and V. A. Kalichevsky, *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 214; *Brit. Chem. Abs.* **B**, 1933, 554; *Chem. Abs.*, 1933, **27**, 3322. *Cf.* H. Siebeneck, *Oel, Kohle, Erdoel, Teer*, 1936, **12**, 793; *Chem. Abs.*, 1936, **30**, 8585; *Brit. Chem. Abs.* **B**, 1936, 1138.

[87] R. Koetschau, *Brennstoff-Chem.*, 1934, **15**, 441; *J. Inst. Pet. Tech.*, 1935, **21**, 122A; *Brit. Chem. Abs.* **B**, 1935, 133; *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 351; *Chem. Abs.*, 1935, **29**, 8307. *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 719; *Brit. Chem. Abs.* **B**, 1935, 1030.

Pulfrich photometer in determining the color of lubricating oils and motor fuels. On the other hand, Bolton and Williams[88] have recommended that the percentage of light transmitted through a 1-inch cell containing the oil may be determined using a photoelectric cell and a galvanometer to measure the current generated. The procedure is to measure the light transmitted when the cell is empty and when it contains the oil. The percentage of light transmitted is defined as 100 times the ratio of the latter to the former. Care must be exercised to exclude all infra-red radiation, as the photoelectric cell is very sensitive to light of long wave length. Results obtained by this procedure were found to be roughly related to Lovibond units (as determined by use of a Lovibond Tintometer).

Ferris and McIlvain[89] measure the depth of oil (or a solution of it) which has the same optical density as the standard filter with which the sample is compared. If R is the depth of oil or solution in mm., N the number of dilutions in a 1:10 ratio, and D the optical density of the neutral filter,[90] then the optical density color is:

$$\frac{10^3 D \times 10^N}{R}$$

The comparison of the sample and filter is carried out using green light which is obtained by interposing a glass cell containing a solution of cupric chloride dihydrate and mercuric chloride between the light source and the mirror in the Duboscq colorimeter. Fig. 292 shows the assembled apparatus, including the shield used to eliminate stray light rays, the colorimeter lamp and filter, the Duboscq colorimeter and the removable shield for the latter. There was found to be a rough correlation between the optical density color and the National Petroleum Association color.[91]

The color of petroleum distillates other than lubricating oils is also of some importance.[92] For example, Rabinovich and Abakova[93] have investigated the color of paraffin wax by comparison of the wax with standard solutions of variable depth.

INORGANIC CONSTITUENTS

The determination of the inorganic constituents of petroleum distillates is not usually necessary in the analysis of lubricating oils,[94] particularly if the latter be completely miscible with naphtha or benzene.[95] The usual procedure is to burn a weighed sample and ignite the residue. The residue is weighed and the ash content calculated from this value.

Schmeling[96] has suggested that, prior to the ignition of a wet oil, the moisture be partially removed by absorption with a filter paper moistened with alcohol. Alcohol is then added to form a layer and the paper used as a taper. Finally, the oil is ignited and the ash weighed. The percentage of alkali metals (sodium and potassium) present in lubricating greases may be ascertained in the following manner. The ash from burning the sample is extracted with hot water and this extract added to oleic acid in ethanol until the solution is alkaline. The alcohol is removed by evaporation, 5 volumes of distilled water are added, and any insoluble calcium soaps filtered off. Alkali metal soaps make this filtrate froth readily and give a precipitate with barium chloride. The alkali metals may be determined quantitatively by converting them to the sulphates, precipitating with barium hydroxide, filtering, and precipitating calcium, strontium and barium with ammonium carbonate. Excess of the latter reagent is destroyed by boiling, and the alkali metals are determined by titration with acid.[97]

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[88] E. R. Bolton and K. A. Williams, *Analyst*, 1935, **60**, 447; *J. Inst. Pet. Tech.*, 1935, **21**, 336A; *Brit. Chem. Abs.* **B**, 1935, 773; *Chem. Abs.*, 1935, **29**, 6475.

[89] S. W. Ferris and J. M. McIlvain, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 23; *Brit. Chem. Abs.* **B**, 1934, 228; *Chem. Abs.*, 1934, **28**, 1513.

[90] Optical density is defined as the ratio of the log of the incident light to transmitted light for the neutral filter.

[91] *Cf.* A.S.T.M. Designation: D155-34T; A.S.A. No.: Z11.34-1935, A.S.T.M. Tentative Standards, American Society for Testing Materials, Philadelphia, 1935.

[92] Color stability is discussed in Chapter 40.

[93] A. M. Rabinovich and E. S. Abakova, *Neft. Khoz.*, 1933, **25** (10), 36; *Rev. pétrolifère*, **1934**, 295; *Chem. Abs.*, 1934, **28**, 4885; *Brit. Chem. Abs.* **B**, 1935, 133.

[94] For discussion of the components of petroleum see Chapter 1.

[95] D. Holde, "Examination of Hydrocarbon Oils and of Saponifiable Fats and Waxes," translated from the German by E. Mueller, John Wiley & Sons, Inc., New York, **1918**.

[96] F. Schmeling, *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 433; *Brit. Chem. Abs.* **B**, 1935, 890; *Chem. Abs.*, 1935, **29**, 8306.

It is sometimes necessary to determine the amount of lead present in greases where it may be present as soaps. Bauer and Ford[98] recommend that 10 g. of the oil be ignited and allowed to burn to dryness in a porcelain crucible. The residue is then heated with sulphuric acid until fuming commences, a few drops of nitric acid are added and heating continued. This is repeated until the residue is white. The lead sulphate is then dissolved in ammonium acetate solution, a small amount of acetic acid being used to dissolve any lead hydroxide that is formed. The solution is filtered, the residue washed with acetic acid and finally with hot water until free from lead. Lead is precipitated from the filtrate by the addition of sulphuric acid. The lead sulphate is filtered onto a Gooch crucible, washed with dilute sulphuric acid, ignited and weighed. Another procedure has been suggested by Levin.[99] This consists essentially in extracting the lead from the oil by heating the latter with a mixture of glacial acetic acid and benzene. Lead is precipitated from the extract by potassium chromate.

Because of the use of tetraethyl lead as an antiknock agent (Chapter 44), it is sometimes necessary to determine its concentration in gasoline. The quantitative methods usually are based upon the decomposition of the lead alkyl by different agents, for example, sulphuric acid,[100] bromine,[101] hydrochloric acid,[102] nitric acid,[103] iodine and sulphur monochloride.[104] In this manner lead is obtained in the form of inorganic salts which in most cases are converted into the sulphate or chromate for gravimetric determination. The use of the spectroscope[105] and of x-rays[106] has also been suggested as agents for the determination of lead in gasoline. The method of Baldeschwieler[107] is said to be somewhat more simple than many others. This depends upon decomposition of the tetraethyl lead by concentrated nitric acid. The procedure is to shake 200 cc. of gasoline with 20 cc. of concentrated nitric acid in a 500 cc. glass-stoppered separatory funnel for 15 minutes. The layers are separated after 2 minutes standing, and 20 cc. of water shaken with the gasoline layer for 15 minutes. The water layer is separated and the washing repeated. The aqueous layers are combined and evaporated to a volume of 20 cc. The solution is cooled and 15 cc. of concentrated sulphuric acid added. This is boiled until fumes of sulphur trioxide appear. Any organic matter is destroyed by the careful addition of nitric acid. After there is no more organic matter present, and the solution has become colorless, the latter is cooled and diluted with 20 to 25 cc. of water and again evaporated to the appearance of sulphur trioxide fumes. It is cooled again and diluted to 150 cc., then cooled in an ice-bath for 1 hour and filtered through a previously ignited and weighed Gooch crucible. The residue (lead sulphate) is washed with 2 per cent sulphuric acid, then with ethanol, dried, ignited and weighed. The grams of lead sulphate per cc. of sample may be multiplied by 2445 to give the number of cc. of tetraethyl lead per gallon of gasoline. The total time for the analysis is said to be about 4 hours.

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[97] R. S. Barnett, *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 183; *Brit. Chem. Abs.* **B**, 1935, 613; *Chem. Abs.*, 1935, **29**, 4285.

[98] A. D. Bauer and C. S. Ford, *Nat. Pet. News*, 1933, **25** (37), 37; *J. Inst. Pet. Tech.*, 1933, **19**, 510A; *Chem. Abs.*, 1933, **27**, 5957.

[99] H. Levin, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 333; *Chem. Abs.*, 1934, **28**, 6584; *Brit. Chem. Abs.* **B**, 1934, 996; *J. Inst. Pet. Tech.*, 1935, **21**, 51A.

[100] S. F. Birch, *J. Inst. Pet. Tech.*, 1924, **10**, 816; *J.S.C.I.*, 1925, **44**, 61B; *Chem. Abs.*, 1925, **19**, 568.

[101] W. R. Ormandy, *J. Inst. Pet. Tech.*, 1924, **10**, 954; *Chem. Abs.*, 1925, **19**, 1194; *J.S.C.I.*, 1925, **44**, 121B. G. Edgar and G. Calingaert, *Ind. Eng. Chem., Anal. Ed.*, 1929, **1**, 221; *Chem. Abs.*, 1929, **23**, 5566; *Brit. Chem. Abs.* **A**, 1929, 1474.

[102] G. Ferreri, *Giorn. chim. ind. applicata*, 1925, **7**, 625; *Brit. Chem. Abs.* **B**, 1926, 181; *Chem. Abs.*, 1926, **20**, 3232.

[103] E. L. Baldeschwieler, *Ind. Eng. Chem., Anal. Ed.*, 1932, **4**, 101; *Chem. Abs.*, 1932, **26**, 1761; *Brit. Chem. Abs.* **B**, 1932, 247.

[104] B. Carli, *Ann. chim. applicata*, 1935, **25**, 634; *Brit. Chem. Abs.* **B**, 1936, 259; *Chem. Abs.*, 1936, **30**, 5389.

[105] G. L. Clarke and H. A. Smith, *J. Phys. Chem.*, 1929, **33**, 659; *Chem. Abs.*, 1929, **23**, 3793; *Brit. Chem. Abs.* **B**, 1929, 504.

[106] R. H. Aborn and R. H. Brown, *Ind. Eng. Chem., Anal. Ed.*, 1929, **1**, 26; *Brit. Chem. Abs.* **B**, 1929, 272; *Chem. Abs.*, 1929, **23**, 1257.

[107] E. L. Baldeschwieler, *loc. cit.*

DETERMINATION OF ACIDITY AND SAPONIFICATION NUMBER

Acid bodies in petroleum products are considered particularly undesirable because of their tendency to corrode the metal parts of machines or containers with which they come in contact. For example, lubricating oil in which acids are present, whether as petroleum acids or sulphuric or sulphonic acids, may effect corrosion of the metal bearings of automobiles.

Acidity may be expressed as the neutralization number, that is, the weight in milligrams of potassium hydroxide required to neutralize one gram of the oil.[108] A sample of the oil is shaken with neutral ethanol and the hot extract titrated with potassium hydroxide using phenolphthalein as an indicator.[109] It is suggested that the mineral acid neutralization number be estimated by extracting the oil several times with hot water and titrating these extracts, employing methyl orange as an indicator. In some instances the aqueous liquid is alkaline, in which case phenolphthalein is substituted for methyl orange, and the alkali neutralization value (milligrams of potassium hydroxide equivalent to the acid used per gram of sample) is ascertained.

Ruibak[110] recommends a somewhat different procedure for inorganic acidity. He uses a reference solution of sodium naphthenates in alcohol of which 20 cc. are added to a 50 g. sample of oil. The alcohol layer is separated after shaking and 5 cc. portions are titrated with 0.1*N* hydrochloric acid. From the known titer of the reference solution it is then possible to calculate the inorganic acidity of the oil as:

$$\text{Per cent sulphuric acid} = a - (20/C)b\,K \times 0.0049 \times 8$$

where *K* is the normality of the hydrochloric acid, *a* is the titer of the sodium naphthenate solution (cc. of standard acid required to neutralize 5 cc.), *b* is the volume of standard acid to neutralize the extract and *C* is the volume of extract.

The presence of acids in oils has been determined also by potentiometric titrations. This has advantages in both accuracy and applicability to opaque liquids. For example, Vellinger[111] has described the use of an antimony electrode for the titration of acid in mineral oil. He suggested the use of a solution of the sample in diethyl ether, ethanol or pentanol. Pavlovskiĭ[112] has outlined a potentiometric method using platinum-hydrogen electrodes. One is placed in a neutral medium, the other in the sample. At zero potential difference, when titrating with alkali, neutralization is complete. Evans and Davenport[113] employ a glass electrode and a silver-silver chloride reference electrode with transformer oils. The arrangement was:

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[108] A.S.T.M. Designation D 188-27T; American Tentative Standard. A.S.A. No. Z11.12-1928; "A.S.T.M. Tentative Standards," American Society for Testing Materials, Philadelphia, Pa., **1935**. See also B. M. Ruibak and N. S. Makushinskaya, *Neft. Khoz.*, 1933, **25**, No. 9, 42; *Chem. Abs.*, 1934, **28**, 4872; *Brit. Chem. Abs.* **B**, 1935, 86; *J. Inst. Pet. Tech.*, 1934, **20**, 448A. F. Wittka, *Olii Min.*, 1934, **12**, 81; *J. Inst. Pet. Tech.*, 1934, **20**, 487A. *Allgemein. Oel- u. Fett-Ztg.*, 1934, **31**, 197; *Chem. Abs.*, 1934, **28**, 5265.

[109] K. R. Dietrich and H. Grassman (*Z. Spiritusind.*, 1935, **58**, 188; *Brit. Chem. Abs.* **B**, 1935, 710) have noted that the use of phenolphthalein in tritration of acids in gasoline is in error because of the presence of carbon dioxide. They recommend methyl red as an indicator.

[110] B. M. Ruibak, *Azer. Neft. Khoz.*, **1935**, No. 4, 81; *Chem. Abs.*, 1935, **29**, 6740; *Brit. Chem. Abs.* **B**, 1936, 818.

[111] E. Vellinger, *Compt. rend. congr. graissage*, **1931**, 117; *Chem. Zentr.*, 1932, **2**, 2575; *Brit. Chem. Abs.* **B**, 1933, 374; *Chem. Abs.*, 1933, **27**, 4913.

Ag, AgCl	Saturated KCl in butanol	Sample in butanol	Glass	.003M Picric acid in butanol	Quinhydrone, Platinum

The butanol was rigorously purified by distillations from potassium hydroxide. α-naphthol, *m*-phenylenediamine hydrochloride and freshly heated lime. Volatile acids were then removed by purging with purified nitrogen for 30 minutes. It was found necessary to have at least 1 per cent of water in the butanol to obtain satisfactory results. A vacuum-tube potentiometer using a galvanometer with sensitivity 4×10^{-10} amperes as null point detector permitted an accuracy of 1 per cent of measured voltage with a current of less than 10^{-15} amperes. The results were plotted as rate of change of voltage per 0.10 cc. of added solution against the volume of added solution. This gave a very sharp maximum at the end point, which could be determined by extrapolation of the curves before and after this point. It was found that the presence of substances such as metallic soaps and peroxides interfered with the accuracy of the results. In the absence of any interfering substances, the accuracy was ±0.001 on the neutralization number as determined on a 20 g. sample.

Saponification number is expressed as the number of milligrams of potassium hydroxide required to react with the esters in 1 g. of oil. The value is usually fairly low for petroleum products. It is determined by saponifying a weighed sample with 25 cc. of standard alkali in the presence of 25 cc. of neutral ethanol. The excess alkali over that required in saponification is determined by titration with $0.5N$ hydrochloric acid.[114]

WATER CONTENT OF PETROLEUM FRACTIONS

The presence of water in lubricating oils or motor fuels is considered undesirable because it tends to separate when the latter are cooled. In an aviation gasoline, for example, this may lead to clogging of the fuel lines and consequent endangerment of life. Some procedures involve separation of water by physical means, e.g., by distillation or centrifugation. Others are based on the reaction of this liquid with some reagent and measurement of the products formed, for example, the liberation of hydrogen by interaction with calcium hydride (see below).

The procedure, recommended by the A.S.T.M.,[115] is that of placing 100 cc. of the oil to be tested in a 500 cc. flask together with an equal volume of water-free gasoline and then distilling the latter. The vapors pass through a delivery tube to which is fused a graduated trap and into a condenser placed above the trap. The condensate flows over the trap, in which water is collected, and the gasoline returns to the flask. Distillation is continued until no more water separates. The volume of water (in cc.) is read from the graduations on the trap. A modification consists in distilling the sample with xylene or toluene and dehydration of the distillate with a weighed amount of anhydrous copper sulphate. The percentage of water can then be calculated from the increase in weight of the copper sulphate. This method is said to be quite flexible in its applicability.[116]

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[112] M. T. Pavlovskii, *Neft Khoz.*, 1935, **28** (3), 75; *J. Inst. Pet. Tech.*, 1936, **22**, 144A; *Chem. Abs.*, 1936, **30**, 3975.

[113] R. N. Evans and J. E. Davenport, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 287; *Chem. Abs.*, 1936, **30**, 6179; *J. Inst. Pet. Tech.*, 1936, **22**, 497A.

[114] A.S.T.M. Designation D 94-28; A.S.A. No. Z 11. 20-1930; A.P.I. No. 514-29, "A.S.T.M. Standards," American Society for Testing Materials, Philadelphia, Pa., **1933**. *Cf.* also G. Elteste, *Chem.-Ztg.*, 1935, **59**, 69; *Brit. Chem. Abs.* **B**, 1935, 293; *Chem. Abs.*, 1935, **29**, 6742. P. Honig and P. J. Klokkers, *Chem. Weekblad*, 1934, **31**, 643; *Chem. Abs.*, 1935, **29**, 3503; *Brit. Chem. Abs.* **B**, 1934, 1092; *J. Inst. Pet. Tech.*, 1935, **21**, 46A. R. Reinhardt, *Compt. rend. congr. graissage*, **1931**, 74; *Chem. Abs.*, 1933, **27**, 4913.

[115] A.S.T.M. Designation D 95-30; A.S.A. No. Z11. 9-1930; A.P.I. No. 519-30; "A.S.T.M. Standards," American Society for Testing Materials, Philadelphia, Pa., 1933.

Another procedure comprises centrifuging the specimen and measuring the volume of water and sediment which separates. This is not entirely satisfactory because the amount of water found is usually lower than the actual amount in the sample.[117]

The determination of water in gasoline by chemical means has been suggested. Thus, Dietrich and Conrad[118] report that it is possible to react the water quantitatively with magnesium nitride. Ammonia is formed by this reaction and is determined by distillation of a portion of the sample into a measured volume of standard acid, followed by titration of the excess acid. This method is said to be applicable even in the presence of alcohols, although some methylamine apparently is formed if there is more than 60 per cent of methanol in the sample. The applicability of the method to the determination of water in petroleum products, as well as many other liquids, has been studied by Boisselet and Rachkani.[119] They found that the procedure is quick and easy, the limiting factor for accuracy being the purity of the magnesium nitride.

By treating the wet sample with substances which will liberate gases, such as hydrogen, the water content may be estimated gasometrically. Thus, Broche and Scheer[120] treated 100 cc. of oil with about 1 g. of calcium hydride and measured the evolved gas. Similarly, Cords[121] has determined the amount of water in a gasoline by measurement of the volume of gas produced by the action of sodium on a liter of the gasoline. This test requires about 48 hours for completion, and is consequently somewhat more time-consuming than the use of calcium hydride.

ANALYSES OF PETROLEUM DISTILLATES BASED ON PHYSICAL CHARACTERISTICS

In addition to the various methods for the analysis of petroleum fractions which depend on the chemical reactivity of one or the other hydrocarbon groups present in various cuts, a number of physical properties or characteristics of the different fractions have been adapted to the estimation of the nature of the distillate.[122]

One of the most common of these physical properties is the vapor pressure, which is measured rather indirectly by distillation tests, either at atmospheric or reduced pressures. Specific gravity is determined for petroleum fractions not necessarily as a characterization factor by itself but because it is of use in conjunction with other characteristics.[122a]

Other properties which are occasionally used are specific refraction, surface

[116] E. Migray, *Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 348; *Brit. Chem. Abs.* **A**, 1935, 1336; *Chem. Abs.*, 1935, **29**, 7223; *J. Inst. Pet. Tech.*, 1935, **21**, 409A.

[117] A.S.T.M. D 96-30; A.S.A. No. Z11.8-1930; A.P.I. No. 520-30; "A.S.T.M. Standards," American Society for Testing Materials, Philadelphia, Pa., 1933.

[118] K. R. Dietrich and C. Conrad, *Z. angew. Chem.*, 1931, **44**, 532; *Chem. Abs.*, 1931, **25**, 4491; *Brit. Chem. Abs.* **B**, 1931, 708.

[119] L. Boisselet and Rachkani, *14me Congr. chim. ind., Paris*, **1934**; *Chem. Abs.*, 1935, **29**, 6018. *Ann. combustibles liquides,* 1935, 10, 449; *J. Inst. Pet. Tech.*, 1935, 21, 337A; *Chem. Abs.*, 1935, **29**, 6727.

[120] H. Broche and W. Scheer, *Brennstoff-Chem.*, 1932, **13**, 281; *Brit. Chem. Abs.* **B**, 1932, 872; *Chem. Abs.*, 1932, **26**, 5196. See also *ibid.*, 1933, **14**, 408; *Chem. Abs.*, 1934, **28**, 1174; *Brit. Chem. Abs.* **B**, 1934, 51.

[121] M. Cords, *Chem.-Ztg.*, 1935, **59**, 288; *Chem. Abs.*, 1935, **29**, 4559; *Brit. Chem. Abs.* **B**, 1935, 536. *Cf.* also W. Scheer, *Chem. Ztg.*, 1935, **59**, 479.

[122] W. L. Nelson, *Refiner,* 1935, **14**, 10, 67; *J. Inst. Pet. Tech.*, 1935, **21**, 88A; *Chem. Abs.*, 1935, **29**, *2701.*

[122a] See, for example, E. S. L. Beale, *J. Inst. Pet. Tech.*, 1937, **23**, 213, 208A.

tension, parachor,[123] and critical solution temperatures. Chilling tests (cloud and pour point) and molecular weight determinations are often carried out on petroleum fractions. The determination of Raman spectra for petroleum distillates has been suggested, although but little used.

Distillation and Vapor Pressure Tests. The analytical procedures which are dependent upon changes in vapor pressure may be classed as (a) evaporation tests; (b) vapor pressure measurement; and (c) distillation tests.

The rate of evaporation of a solvent is well known to be of importance in connection with the properties of paints and other protective coatings. Too high a rate results in cooling during drying and condensation of moisture on the surface of the coating. This may result in "blushing." In motor fuels, too rapid evaporation or too great volatility may result in vapor lock.[124] (See Chapter 44.)

The measurement of vapor pressure has been effected in several ways. The A.S.T.M. method[125] depends upon volatilization of the gasoline being tested in a cylinder equipped with a pressure gauge. The determination may be carried out at temperatures from 32° to 110°F. and corrected to give the value at 100°F. (Reid vapor pressure) by means of tables.[126] Lederer has shown that vapor pressure, p, at temperature, T, may be calculated from the equation:

$$\log\frac{pS}{p} = (q/4.571)\,(T^{-1} - TS^{-1})$$

where T_S is boiling point at atmospheric pressure, p_S, and q is molar heat of vaporization.[127] By consideration of his experimental results, he concluded that there was some relationship between vapor pressure and both viscosity and flash-point.

Distillation has long been used to indicate the degree of purity of organic compounds. The distillation of various of the lighter petroleum fractions is regularly undertaken as an indication of their nature.[128] By plotting the volume of distillate against the temperature of distillation and connecting the points, curves are obtained which are spoken of as "distillation curves." The various points on this curve have been used as indications of the nature of the fuel in practice. The 10 per cent point, for example, is considered to be an indication of the ease of starting.[129] The quick warming-up characteristics are indicated by the 35 per cent point and steady driving by the 60 per cent point. It is also possible to determine the content of butanes, pentanes, hexanes, and higher homologues from the Engler (A.S.T.M.) distillation curve of a gasoline. This is accomplished by reference to empirically determined graphical relationships.

For substances which are relatively volatile, such as gasoline and kerosene, it is possible to conduct distillations under atmospheric pressure. On the other hand, the low volatility of heavy stocks e.g., lubricating oils, precludes their distillation except under rather high vacuum.[130] Schicktanz[131] suggested an apparatus for the accurate determination of boiling points of lubricating oils and other high boiling substances. Three thermocouples are placed at different heights in the fractionating column. For a pure substance their readings should be the same, and the difference between their readings is a qualitative indication of the purity of the substance. Watson and Wirth[132] have outlined a procedure for the distillation of oils under a pressure of about 0.1 mm. of mercury. The sample (200 cc.) is first distilled under atmospheric pressure up to 500°F. A portion of the bottoms from this distillation equivalent to 100 cc. of the original oil is then distilled under reduced pressure. From the boiling range data for the latter distillation, it is possible to obtain the boiling range at normal pressure by the use of a nomogram.[133]

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[123] See latter part of this chapter.

[124] *Cf.* O. Herstad, *Petroleum Z.*, 1934, **30**, No. 10; *Motorenbetrieb und Maschinen-Schmierung*, **7**, 2; *Chem. Abs.*, 1934, **28**, 4850; *Brit. Chem. Abs.* **B**, 1934, 353. G. G. Brown, *Univ. Mich., Eng. Research Bull.*, 1930, No. **14**; *Chem. Abs.*, 1930, **24**, 4924. *Proc. 12th Ann. Conv. Nat. Gasoline Assoc.*, **1933**, 64; *J. Inst. Pet. Tech.*, 1934, **20**, 312A. R. E. Wilson, *Oil Gas J.*, 1930, **29**, No. 9, 40, 98, 100; No. 10, 38, 127; *Am. Soc. Testing Materials,* March, **1930**; *Chem. Abs.*, 1930, **24**, 4924. N. Fuchs, *Z. angew. Chem.*, 1931, **44**, 962; *J. Applied Chem.* (*U.S.S.R.*), 1931, **4**, 678; *Chem. Abs.*, 1932, **26**, 1426. K. Hachmuth, *Ind. Eng. Chem.*, 1932, **24**, 82; *Brit. Chem. Abs.* **B**, 1932, 376; *Chem. Abs.*, 1932, **26**, 1169.

[125] A.S.T.M. Designation D 417-35T, D 323-32T; "A.S.T.M. Tentative Standards," American Society for Testing Materials, Philadelphia, Pa., **1935**.

[126] See also R. Salmoni, *Giorn. chim. ind. appl.*, 1934, **16**, 483; *J. Inst. Pet. Tech.*, 1935, **21**, 46A; *Chem. Abs.*, 1935, **29**, 2716. T. F. G. Noyd and H. J. Jones, *Petroleum Eng.*, 1930, 1, No. 13, 40, 42; *Chem. Abs.*, 1930, **24**, 5472. *Cf.* R. R. Crippen and F. N. Laird, *Refiner,* 1934, **13**, 106; *Chem. Abs.*, 1934, **28**, 3880; *Brit. Chem. Abs.* **B**, 1934, 867.

[127] E. L. Lederer, *Petroleum Z.*, 1935, **31**, No. 16, 3; *Chem. Abs.*, 1936, **30**, 2816; *Brit. Chem. Abs.* **B**, 1935, 613.

[128] For the procedure see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. "A.S.T.M. Standards," American Society for Testing Materials, Philadelphia, Pa., **1933**.

[129] *Cf.* M. G. Blair and R. C. Alden, *Ind. Eng. Chem.*, 1933, **25**, 559; *Brit. Chem. Abs.* **B**, 1933, **533**.

Steam-distillation at constant temperature has been proposed as a method for determining the volatility range of high-boiling petroleum fractions. The operation is carried out at a temperature between 320 and 350°C., and the proportion of oil in the distillate is ascertained at regular temperature intervals. Plotting temperature against volume of distillate gives a step-like curve. By connecting the mid-points of the horizontal portions of the curve, a line is obtained which represents fairly closely the volatility curve for the oil.[134]

Flash Point. The flash point of an oil may be defined as the temperature at which an oil evaporates so intensively that its vapor, in an open space of specified dimensions or in a specified container, forms an ignitable mixture with air. The flash point is of value in indicating the fire hazard resulting from the storage or employment of the oil. The "burning point" is also of importance in this connection. The latter is the temperature at which the vapors not only flash but continue to burn.[135] The lower these two temperatures, the greater the danger of the oil volatilizing sufficiently to form an explosive mixture with the surrounding air.

The methods by which flash-point may be determined specify the conditions under which the test is to be performed quite closely because of the influence of the dimensions of the space in which the flash occurs upon the flash-point. One form of apparatus is the Cleveland Open Cup which has been adopted by the A.S.T.M.[136] The oil to be tested is heated in a standard cup at a rate of about 10°F. per minute as the temperature approaches the probable flash-point. When the temperature of the oil passes every 5°F. mark on the thermometer immersed in it, a test flame of specified dimensions is applied to the sample. The results obtained by this test may be evaluated only in terms of other tests.[137] The other forms of apparatus consist essentially of a closed cup. Examples of this type are the Abel Tester, the Tag Closed Tester and the Pensky-Martens Closed Tester. The latter two are standard in the United States for volatile flammable liquids (boiling below 175°F.) and fuel oils, respectively. The Abel Tester was specified for use in the examination of petroleum products by The Petroleum Act of 1879.[138] In general, it is very similar to both the Pensky-Martens and Tag closed testers, in which the oil sample is heated and its vapors intermittently exposed to a flame of certain dimensions.[139]

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[130] Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. See also H. Bruckner, *Gas- und Wasserfach*, 1934, 77, 58; *Brit. Chem. Abs* **B**, 1934, 309; *Chem. Abs.*, 1934, **28**, 2155. E. L. Lederer, *Petroleum Z.*, 1935, **31**, No. 6, 1; *Chem Abs.*, 1935, **29**, 5637; *Brit. Chem. Abs.* **B**, 1935, 709 K. M. Watson and E. F. Nelson, *Ind. Eng Chem.*, 1933, **25**, 880; *Brit. Chem. Abs.* **B**, 1933, 995; *Chem. Abs.*, 1933, **27**, 5522.

[131] S. T. Schicktanz, *J. Research Natl. Bur. Standards*, 1935, **14**, 685; *Chem. Abs.*, 1935, **29**, 6106.

[132] K. M. Watson and C. Wirth, III, *Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 72; *Chem. Abs.*, 1935, **29**, 1972; *Brit. Chem. Abs.* **B**, 1935, 259.

[133] A nomogram or nomograph is a comparison of related properties by means of graduated lines The lines may or may not be straight and the gradations need not follow a regular scale. See for the construction of such charts, H. V. Beck, *Petroleum Engr.*, 1931, **3**, No. 3, 67; *Chem. Abs.*, 1932, **26**, 6110.

[134] R. N. J. Saal and C. G. Verver, *J. Inst. Pet. Tech.*, 1933, **19**, 336; *Brit. Chem. Abs.* **B**, 1933, 612; *Chem. Abs.*, 1933, **27**, 5526.

[135] See T. B. Stillman, "The Examination of Lubricating Oils," The Chemical Publishing Co., Easton, Pa., **1914**. A. H. White, "Technical Gas and Fuel Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., **1913**. W. A. Hamor and F. W. Padgett. "The Technical Examination of Crude Petroleum, Petroleum Products and Natural Gas," McGraw-Hill Book Co., Inc., New York, N. Y., **1920**. J. A. Hicks and A. W. Cox, "The Laboratory Book of Mineral Oil Testing," Chas. Griffin & Co., Ltd., London, **1925**.

[136] A.S.T.M. D. 92-33; A.S.A. No. Z11. 6-1933; A.P.I. No. 511-33; "A.S.T.M Standards," American Society for Testing Materials, Philadelphia, Pa., **1933**.

[137] S. Erk, *Erdöl und Teer*, 1933, **9**, 122; *Chem. Abs.*, 1933, **27**, 3809.

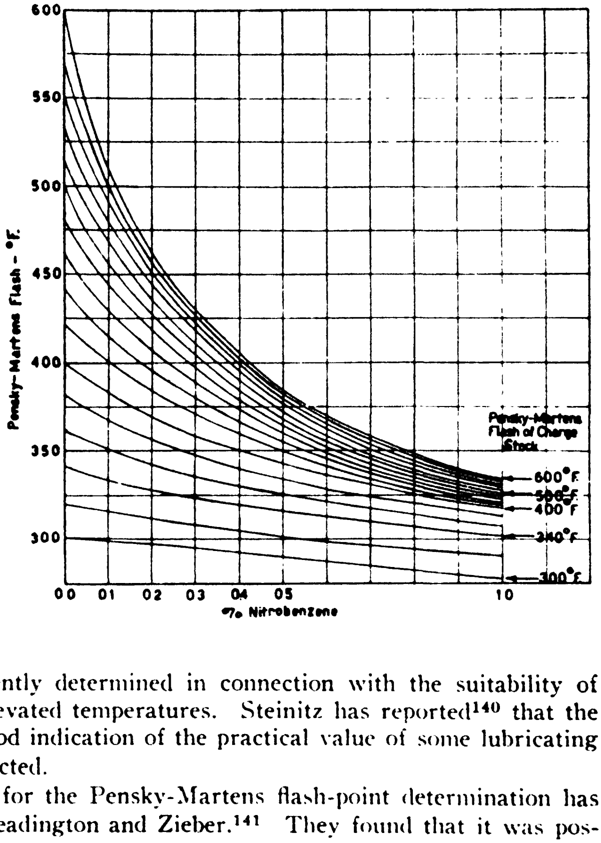

FIG. 293.
Chart for Determination of Nitrobenzene Content of Mixtures with Hydrocarbon Oils by Measurement of Flash Points. (S. S. Kurtz, Jr., C. E. Headington and B. Zieber)

Courtesy Industrial and Engineering Chemistry

The flash-point is frequently determined in connection with the suitability of lubricating oils for use at elevated temperatures. Steinitz has reported[140] that the flash-point did not give a good indication of the practical value of some lubricating oils in tests which he conducted.

A rather interesting use for the Pensky-Martens flash-point determination has been suggested by Kurtz, Headington and Zieber.[141] They found that it was possible to determine the amount of nitrobenzene present in the raffinate from the solvent-refining of lubricating oils using nitrobenzene. This method is applicable only to oils flashing between 300 and 600°F. (149° and 316°C.) which contain 1 per cent or less of nitrobenzene. The procedure involves ascertaining the flash-point of the oil before treatment and then of the raffinate containing nitrobenzene. By means of the curves shown in Fig. 293 the per cent of nitrobenzene may be read off. For example, if the original flash-point was 440°F. and the flash-point of the sample containing nitrobenzene was 330°F., by reference to the chart it is found that there is 0.83 per cent of nitrobenzene in the sample.

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[138] This method is summarized, together with the other early procedures, in A. H. Allen, "Commercial Organic Analysis," 3rd Ed., revised by H. Leffmann, P. Blakiston's Son & Co., Philadelphia, Pa., 1900.

[139] Flash-Point by Means of the Pensky-Martens Closed Tester, A.S.T.M. Designation D 93-22; A.S.A. No. Z11. 7-1928; A.P.I. No. 510-29; "A.S.T.M. Standards," American Society for Testing Materials, Philadelphia, Pa. **1933**. Also Tentative Revision, page 1527, "A.S.T.M. Tentative Standards," Philadelphia, Pa., **1935**. Tentative Method of Test for Flash Point by Means of the Tag Closed Tester, A.S.T.M. Designation, D 56-35T, "A.S.T.M. Tentative Standards," Philadelphia, Pa., **1935**, 713. See also R. A. Randall, *Ind. Chemist*, 1933, **9**, 91; *Brit. Chem. Abs.* **B**, 1933, 376; *Chem. Abs.*, 1933, **27**, 4913.

[140] E. W. Steinitz, *Petroleum Z.*, 1934, **30**, No. 41; *Motor u. Maschinen Schmierung*, 1934, **7**, No. 10, 5; *Chem. Abs.*, 1935, **29**, 588; *Brit. Chem. Abs.* **B**, 1934, 997. See also H. Hassenbach, *Wärme*, 1930, **53**, 444; *Chem. Abs.*, 1930, **24**, 5474.

[141] S. S. Kurtz, Jr., C. E. Headington and B. Zieber, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 1; *Brit. Chem. Abs.* **B**, 1936, 355; *Chem. Abs.*, 1936, **30**, 2358.

Determination of Molecular Weight. There are three common procedures for the estimation of molecular weight, viz., the vapor pressure, cryoscopic and ebullioscopic methods. These are characterized by rather limited applicability. The vapor pressure method of Victor Meyer is rather difficult to apply to substances of high boiling point, although Nernst[142] has designed an apparatus of pure iridium which he used up to more than 2000°C. The method is to weigh out a small amount of the sample, which is then introduced into a vessel where it can be heated so that it is completely vaporized. By measurement of the increase in volume, the temperature and pressure and application of the ideal gas laws, it is then quite simple to calculate the molecular weight of the unknown. This method has been recommended by Newman and Meanes.[143]

Cryoscopic methods have the disadvantage that many substances tend to crystallize out of the solvent medium on cooling. On the other hand, there is less likelihood of loss of the sample through volatilization. A number of compounds have been recommended as the liquid media in the determination of molecular weights by this procedure. Camphor is quite satisfactory in many instances,[144] although benzene is widely employed[145] as is also nitrobenzene. In some cases where peculiarities of the material under investigation make the above solvents unsatisfactory, dioxane and ethylene dibromide have been used.[146] Fenske, McCluer and Cannon[147] suggested cyclohexane as a solvent and found that values secured with this liquid checked fairly satisfactorily with results obtained by computations from molal heats of vaporization.

The ebullioscopic method for molecular weight determination has the disadvantage of loss of sample by volatility. Mair[148] has observed that extrapolation of the results to infinite dilution for purposes of calculation gives values that agree with theory rather well. This was done by determination of several values for the boiling point elevation using different concentrations of the solute, and plotting these against concentration. Extrapolation was then very easily effected.

Viscosity. The determination of viscosity has long been one of the standard procedures in the control of petroleum products, particularly the higher boiling fractions which are used as lubricants.[149] The most common methods for the measurement of viscosity depend upon the relationship established by Poiseuille[149a]:

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[142] W. Nernst, *Z. Elektrochem.*, 1903, **9**, 622; *J.C.S.*, 1903, **84**, 636.

[143] E. L. Newman and E. A. Meanes, *Refiner*, 1935, **14**, 432; *Chem. Abs.*, 1935, **29**, 7717. See also, J. B. Niederl, O. R. Trautz and A. A. Plentl, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 252; *J. Inst. Pet. Tech.*, 1936, **22**, 495A; *Chem. Abs.*, 1936, **30**, 6255.

[144] See, among other sources of information, J. Eggert, "Physical Chemistry," translated by S. J. Gregg, D. Van Nostrand Co., Inc., New York, 1933.

[145] O. FitzSimons and E. W. Thiele, *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 11; *J. Inst. Pet. Tech.*, 1935, **21**, 122A; *Chem. Abs.*, 1935, **29**, 1972. M. Lerer, *Ann. combustibles liquides*, 1934, **9**, 511; *Chem. Zentr.*, 1934, **2**, 2636; *Brit. Chem. Abs.* **B**, 1935, 536; *Chem. Abs.*, 1934, **28**, 6285; *J. Inst. Pet. Tech.*, 1934, **20**, 481A. H. T. Rall and H. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 324, 436; *Brit. Chem. Abs.* **B**, 1936, 1076; *Chem. Abs.*, 1936, **30**, 7825.

[146] M. Lerer, *loc. cit.* E. R. Epperson and H. L. Dunlap, *Ind. Eng. Chem.*, 1932, **24**, 1369; *Chem. Abs.*, 1933, **27**, 834; *Brit. Chem. Abs.* **B**, 1933, 137.

[147] M. R. Fenske, W. B. McCluer and M. R. Cannon, *Ind. Eng. Chem.*, 1934, **26**, 976; *Chem. Abs.*, 1934, **28**, 6988; *Brit. Chem. Abs.* **B**, 1934, 1047.

[148] B. J. Mair, *J. Research Natl. Bur. Standards*, 1935, **14**, 345; *Chem. Abs.*, 1935, **29**, 4555; *J. Inst. Pet. Tech.*, 1935, **21**, 198A.

$$V = \frac{\pi g p R^4 t}{8 l \eta}$$

where V is the volume of oil of viscosity, η, which passes through a capillary tube of radius, R, and length, l, in time, t, under pressure, p, when g is the acceleration due to gravity.[150] The instrument to be used is so constructed and the conditions of the experimental determination so fixed that:

$$\eta = (C)t$$

where C includes all the other terms of the equation. Some of the methods which involve this generalization are the Engler, Saybolt, Redwood, Barbey, Lamansky-Nobel[151] and many others.[152] The general procedure is to time the flow of oil through a capillary of standard dimensions until a given volume of oil has been collected in a calibrated flask. In the Saybolt Universal and Furol Viscosimeters, also known as viscometers, this volume is 60 cc.,[153] though in the Engler viscometer it may be 50, 100 or 200 cc. depending upon the viscosity of the oil.[154]

Viscosity is of two kinds, namely, dynamic, which is expressed in poises, and kinematic,[155] which is expressed in stokes. The relationship, where P is dynamic and K kinematic viscosity and d the density of the substance, is

$$P = K/d$$

Relationships between these absolute units and the arbitrary units such as Saybolt seconds, Engler degrees and Redwood seconds have been established by various workers.[156] The relationships vary somewhat in different ranges of viscosity.

[149] Although most physical properties of mixtures are additive and follow the rule of mixtures, A. N. Hartmann (*3rd Collection of Articles of the Inst. of Materials of People's Commissariat of Communication (Moscow)*, 1929, Issue **8**/112, 40; *Chem. Abs.*, 1930, **24**, 5472) has observed that this was not true of the viscosities of creosote-fuel oil mixtures. For a method of plotting viscosity gravity constants against volume per cent of solvent in an extract to obtain regions of complete and partial miscibility, see S. S. Kurtz, Jr., *Ind. Eng. Chem.*, 1935, **27**, 845; *Chem. Abs.*, 1935, **29**, 5311; *Brit. Chem. Abs.* **B**, 1935, 753.

[149a] Poiseuille, *Compt. rend.*, 1842, 15, 1167; *Ann. chim. phys.*, 1843, 7 (3), 50; *Pogg. Ann.*, 1843, **58**, 424; *Ann.*, 1848, **64**, 129.

[150] See E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill Book Co., New York, **1922**, for a discussion of this equation and its derivation.

[151] This viscometer has been used in Russia. For a description see R. Wischin, *Chem. Rev. Fett Harz-Ind.*, 1896, **4**, 75, 89; *Chem. Zentr.*, 1897, 1, 890, 1136. L. Singer, *Chem. Rev. Fett. Harz-Ind.*, 1896, **4**, 243; *Chem. Zentr.*, 1897, 2, 1041.

[152] Enumeration and description of the many variations in viscometer design are beyond the scope of this work. See E. C. Bingham, *loc. cit.* See also L. Squires and R. L. Dockendorff, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 295; *Chem. Abs.*, 1936, **30**, 5462; *Brit. Chem. Abs.* **A**, 1936, 1085; *J. Inst. Pet. Tech.*, 1936, **22**, 496A.

[153] A.S.T.M. Designation D 88-33; A.S.A. No. Z11. 2-1933; A.P.I. No. 518-33; "A.S.T.M. Standards," American Society for Testing Materials, Philadelphia, Pa., **1933**. *Cf.* T. G. Delbridge, *Refiner*, 1934, **13**, 461; *Chem. Abs.*, 1935, **29**, 2715; *J. Inst. Pet. Tech.*, 1935, **21**, 88A.

[154] D. Holde and E. Mueller, "The Examination of Hydrocarbon Oils," John Wiley & Sons, Inc., New York, **1915**. According to F. H. Garner and W. E. J. Broom (*Rev. pétrolifère*, 1935, No. **647**, 1204; *J. Inst. Pet. Tech.*, 1936, **22**, 27; *Chem. Abs.*, 1936, **30**, 1624; *Oel, Kohle, Erdoel, Teer*, 1936, **12**, 77) the Engler instruments are less accurate than either the Redwood or Saybolt.

[155] G. Barr (*Proc. World Petr. Congr.*, 1933, **2**, 508; *J. Inst. Pet. Tech.*, 1934, **20**, 296A; *Chem. Abs.*, 1934, **28**, 4887; *Brit. Chem. Abs.* **B**, 1934, 656) has suggested the word "lentor" as a name for kinematic viscosity. Dynamic or absolute viscosity is the expression of the internal friction of fluids in absolute units. The unit employed is the poise, or force in dynes per sq. cm. required to move a surface of 1 sq. cm. at a velocity of 1 cm. per sec. past an equal surface 1 cm. distant, when the space between surfaces is filled with the fluid under investigation. Kinematic viscosity is the quotient, in stokes, of the dynamic viscosity divided by the density of the fluid. See V. A. Kalichevsky and B. A. Stagner, "Chemical Refining of Petroleum," The Chemical Catalog Co., Inc., New York, **1933**. W. H. Walker, W. K. Lewis, and W. H. McAdams, "Principles of Chemical Engineering," McGraw-Hill Book Co., Inc., New York and London, **1923**. A. W. Nash and A. R. Bowen, "The Principles and Practice of Lubrication," Chapman & Hall, Ltd., London, **1929**.

[156] See, for example, F. H. Garner and C. I. Kelly, *Physics*, 1933, **4**, 97; *Petroleum Z.*, 1933, **29** (28), 1; *Chem. Abs.*, 1934, **28**, 621; *Brit. Chem. Abs.* **B**, 1933, 767. Also *Compt. rend. congr. graissage*, **1931**, 475; *Brit. Chem. Abs.* **B**, 1933, 287; *Chem. Zentr.*, 1932, **2**, 2906. Also W. B. McCluer and M. R. Fenske, *Ind. Eng. Chem.*, 1935, **27**, 82; *Brit. Chem. Abs.* **B**, 1935, 613; *J. Inst. Pet. Tech.*, 1935, **21**, 87A; *Chem. Abs.*, 1935, **29**, 1971. F. H. Garner, W. E. J. Broom and J. L. Taylor, *J. Inst. Pet. Tech.*, 1936, **22**, 11; *Chem. Abs.*, 1936, **30**, 2818. L. Ubbelohde, *Chem.-Ztg.*, 1907, **31**, 38; *Chem. Abs.*, 1907, 1, 1087. *Cf.* I. D. Afanasyev, *Neft. Khoz.*, 1929, **17**, 218; *Brit. Chem. Abs.* **B**, 1930, 402; *Chem. Abs.*, 1930, **24**, 952.

The various arbitrary units are also interchangeable by the application of suitable equations.

An instrument which is also based on the rate of flow of an oil through a capillary tube is the Ostwald viscometer. Willihnganz and his co-workers[157] have described a modification of this instrument which is said to be more satisfactory than the usual type. An Ostwald viscometer which can be used for the measurement of the viscosity of tar has been suggested by Lee.[158] Ubbelohde[159] has described a "suspended-level" viscometer which is reported to be an improvement over the usual instruments in several ways, such as the replacement of the lower liquid level by a suspended level.

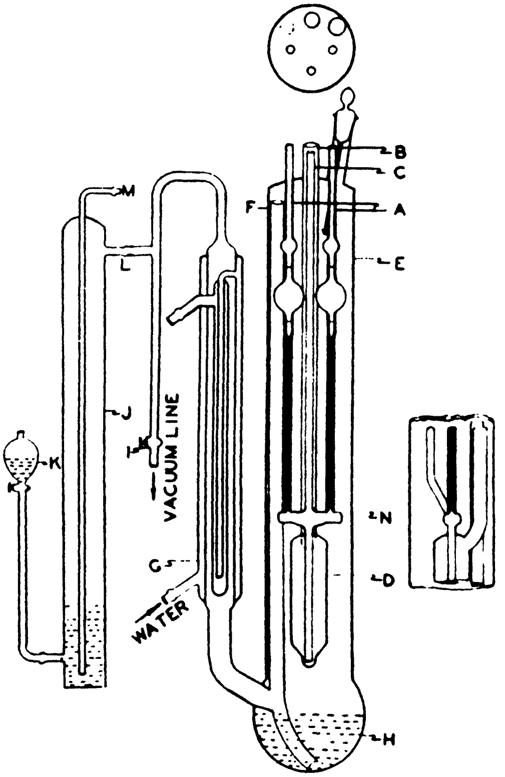

FIG. 294. Modified Form of Ubbelohde Capillary Viscometer. (O. Fitz-Simons)

A. Capillary tube
B. Tube
C. Air vent
D. Oil reservoir
E. Vapor bath
F. Riser
G. Condenser
H. Bulb
I. Valve
J. Column
K. Leveling bottle
L, N. Tubes

Courtesy Industrial and Engineering Chemistry

A modified form of the Ubbelohde suspended-level viscometer has been designed by FitzSimons.[160] This instrument is said to surpass the more ordinary types of viscometer in speed, accuracy, and in ease of operation. The apparatus is shown in Fig. 294. The description of the apparatus and procedure is:

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[157] E. A. Willihngauz, W. B. McCluer, M. R. Fenske and R. V. McGrew, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 231; *Chem. Abs.*, 1934, **28**, 5971; *Brit. Chem. Abs.* **B**, 1934, 788. See also E. A. Willihnganz, *Physics*, 1934, **6**, 61; *J. Inst. Pet. Tech.*, 1935, **21**, 124A; *Chem. Abs.*, 1935, **29**, 3501. See also M. R. Fenske and W. B. McCluer, *Refiner*, 1934, **13**, 215; *Chem. Abs.*, 1934, **28**, 5651; *J. Inst. Pet. Tech.*, 1934, **20**, 444A. Also *Nat. Pet. News*, 1936, **28** (29), 25; *J. Inst. Pet. Tech.*, 1936, **22**, 496A.

[158] A. R. Lee, *J.S.C.I.*, 1934, **53**, 69T; *Chem. Abs.*, 1934, **28**, 3221; *Brit. Chem. Abs.* **B**, 1934, 307; *J. Inst. Pet. Tech.*, 1934, **20**, 297A.

[159] L. Ubbelohde, *J. Inst. Pet. Tech.*, 1933, **19**, 376; *Chem. Abs.*, 1933, **27**, 4719; *Brit. Chem. Abs.* **B**, 1933, 607. *Ibid.*, 1936, **22**, 32; *Chem. Abs.*, 1936, **30**, 2426. See also *Proc. World Petr. Congr.*, 1933, **2**, 496. *Cf.* British P. 400,840, 1933, to Glasplakatefabrik Union G.m.b.H.; *J. Inst. Pet. Tech.*, 1934, **20**, 27A; *Chem. Abs.*, 1934, **28**, 1895. L. Ubbelohde, *Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 85.

> The apparatus consists of two capillaries of different sizes, A, sealed into a vapor bath, E. "Tube C is an air vent for producing the suspended level and tube B is connected to the oil reservoir, D.
>
> "The bulb is filled with a pure organic liquid with a normal boiling point slightly above the temperature at which it is desired to operate the viscometer, methylene chloride being suitable for use at 37.78°C. (100°F.) and tertiary amyl alcohol for use at 98.89°C. (210°F.). Vacuum is turned on and regulated by Valve I to obtain a slow rise of bubbles up Column J. The bulb, H, is heated electrically causing vapor to rise up the jacket and down the riser, F, to the condenser, G, and return as liquid to the bulb, H. To obtain exactly the desired temperature, the pressure is adjusted by adding or removing water from the pressure-regulating column, J, by means of the leveling bottle, K. By changing the connection to the column from Tube L to Tube M and substituting an air line for the vacuum line, the viscometer can be operated under pressure; this is occasionally necessary on days of low barometer.
>
> "Oil is poured through a 100-mesh filter down Tube B until reservoir D is about one-half full; this requires about 12 cc. After a short wait of 1 to 2 minutes to allow the oil to reach bath temperature, Tube C and the smaller capillary, A, are closed off with the fingers and oil is drawn up into the right capillary by suction well above the upper mark. The suction line and fingers are then removed, establishing the suspended level at N, and the time for the oil to pass between the marks is noted. If the time is less than 100 seconds the oil is immediately drawn up into the smaller (left) tube and the efflux time observed. The kinematic viscosity is obtained by multiplying the efflux time by a factor determined by calibrating each tube of the instrument on an oil of known viscosity. At short efflux times a kinetic energy correction is necessary, which is always less than 1 per cent for motor oils. The kinetic energy correction is calculated from the dimensions of the instrument.
>
> "The oil is quickly removed through Tube C by a suction line connected to a trap. The instrument is flushed with a narrow cut naphtha with an initial slightly above the bath temperature. The naphtha is also removed by suction through Tube C and the instrument sucked dry. The entire cleaning operation requires about one minute."

Other methods which have been used for the determination of viscosity include the falling sphere[161] and its modification in which a bubble is permitted to rise through the liquid.[162] Another variation consists of permitting spheres of known dimensions to fall through a column of the oil which is somewhat inclined.[163] A method which is analogous to the falling sphere method is that described by Duffing.[164] In his method, using what he calls a viscometric balance, a sphere rises a known distance through a liquid under the influence of a force applied by means of a weight on the other arm of the balance. The results from this apparatus are calculated directly in centipoises. Yet another viscometer is that which has been advocated by Smith[165] and employed by him in studying the effect of carbon suspensions on the properties of lubricating oils. The method consists essentially in counting by means of a photo-electric cell the number of drops falling from an orifice.

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[160] O. FitzSimons, *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 345; *J. Inst. Pet. Tech.*, 1936, **22**, 90A; *Brit. Chem. Abs.* **A**, 1935, 1342; *Chem. Abs.*, 1936, **30**, 2050. Another modification of the suspended-level viscometer is described by F. H. Payne and C. C. Miller, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 300; *J. Inst. Pet. Tech.*, 1936, **22**, 496A; *Chem. Abs.*, 1936, **30**, 5403.

[161] *Cf.* E. J. Harris, *Ind. Chem.*, 1934, **10**, 139; *Chem. Abs.*, 1934, **28**, 3942; *J. Inst. Pet. Tech.*, 1934, **20**, 403A; *Brit. Chem. Abs.* **B**, 1934, 507. F. Hirata and K. Kubo, *J. Soc. Chem. Ind. Japan*, 1934, **37** (1), 11B; *J. Inst. Pet. Tech.*, 1934, **20**, 297A; *Brit. Chem. Abs.* **A**, 1934, 385; *Chem. Abs.*, 1934, **28**, 1911. E. S. L. Beale and P. Docksey, *J. Inst. Pet. Tech.*, 1936, **22**, 42; *Chem. Abs.*, 1936, **30**, 2050; *J. Inst. Pet. Tech.*, 1936, **22**, 89A. A micro-method for the determination of viscosity on the rolling-ball principle has been designed by H. F. Schneider, Jr., and T. A. McConnell, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 28; *Chem. Abs.*, 1936, **30**, 1558. This method was devised for the study of oil in the insulation of cables.

[162] L. Steiner, *Proc. World Petr. Congr.*, 1933, **2**, 483; *J. Inst. Pet. Tech.*, 1934, **20**, 233A; *Chem. Abs.*, 1934, **28**, 4887; *Petroleum Z.*, 1934, 20 (6); *Motorenbetrieb u. Maschinen-Schmierung*, 1934, 7, 2; *Brit. Chem. Abs.* **B**, 1934, 744. See also O. S. Panyatin and O. S. Obleukhova, *Neft. Khoz.*, 1933, **25**, 105; *J. Inst. Pet. Tech.*, 1934, **20**, 444A.

[163] F. Höppler, *Proc. World Petr. Congr.*, 1933, **2**, 503; *Chem. Abs.*, 1934, **28**, 4887. See also, *Chem. Met. Eng.*, 1935, **42** (12), 687.

[164] G. Duffing, *Proc. World Petr. Congr.*, 1933, **2**, 499; *Chem. Abs.*, 1934, **28**, 4887.

[165] H. H. Smith, *Instruments*, 1935, **8** (7), 170; *Chem. Abs.*, 1935, **29**, 6749; *J. Inst. Pet. Tech.*, 1935, **21**, 374A.

The Expression of the Temperature Variation of Viscosity. In the previous discussion of viscosity it has been pointed out that viscosity is commonly expressed in either absolute units, such as poises or stokes, or in arbitrary units such as the Saybolt second or Engler degrees. These measurements give an indication of the viscosity only at the specified temperature at which they were determined. Numerous methods have been suggested by which it would be possible to indicate by means of one value the extent to which viscosity changes at rising temperatures. One of these methods was the ratio of the viscosities at 100 and 210°F. The Viscosity Index was first suggested by Dean and Davis[166] as a method for evaluating the variation of viscosity with temperature and was later discussed by Davis, Lapeyrouse and Dean and others.[167] To determine the viscosity index (V.I.) of an oil it is compared with two other oils whose viscosities at 210°F. are the same as the unknown. The two standard oils are chosen from such a stock that they differ widely in viscosity at 100°F. If the unknown has a viscosity V at 100°F., and the standards, viscosities of L and H at 100°F. for oils of poor and good (Gulf Coast and Pennsylvania base) qualities, respectively, the viscosity index is then given by the equation,

$$\text{V.I.} = \frac{L - V}{L - H} \times 100$$

Thus, an oil which compares favorably with oils of Pennsylvania origin and has relatively low change of viscosity with temperature will have a V.I. near 100, and an oil with wide variation in viscosity with temperature will have a V.I. near zero.

Other methods have been suggested for representation of change of viscosity such as the Viscosity Gravity constant of Hill and Coats,[168] the Gravity-Index[169] and numerous other systems.[170]

Tests for Cloud and Pour Points. The cloud point of a petroleum oil is defined as "the temperature at which paraffin wax or other substances begin to crystallize or separate from solution when the oil is chilled under definite prescribed conditions."[171] "The pour point of a petroleum oil is the lowest temperature at which the oil will pour or flow when it is chilled without disturbance under definite prescribed conditions." It has been observed that cloudiness may be due to water, soaps, sodium sulphate or ceresin.[172] The pour point and cloud point depend to some extent upon the treatment which the oil has undergone. Heating the oil, even only above 100°F., makes it necessary to wait some time before testing. There is some tendency for asphaltenes to keep wax in solution in this determination, particularly if there is any pronounced agitation during cooling.

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[166] E. W. Dean and G. H. B. Davis, *Chem. Met. Eng.*, 1929, **36**, 618; *Chem. Abs.*, 1930, **24**, 716; *Brit. Chem. Abs.* **B**, 1929, 1039.

[167] G. H. B. Davis, M. Lapeyrouse and E. W. Dean, *Oil Gas J.*, 1932, **30** (46), 92; *Chem. Abs.*, 1932, **26**, 6112. See also I. L. Newell, *Ind. Eng. Chem.*, 1931, **23**, 843; *Brit. Chem. Abs.* **B**, 1931, 829; *Chem. Abs.*, 1931, **25**, 4392. H. G. Nevitt, *Petr. Eng.*, 1933, **5** (3), 28; *J. Inst. Pet. Tech.*, 1934, **20**, 155A. L. Ivanovszky, *Petroleum Z.*, 1934, **30** (42), 1; *Chem. Abs.*, 1935, **29**, 2715; *Ibid.*, 1935, **31** (2), 1; *Chem. Abs.*, 1935, **29**, 6745; *Brit. Chem. Abs.* **B**, 1935, 289. P. Docksey, C. H. G. Hands and W. A. Hayward, *J. Inst. Pet. Tech.*, 1934, **20**, 248; *Chem. Abs.*, 1934, **28**, 4579; *Brit. Chem. Abs.* **B**, 1934, 390; *J. Inst. Pet. Tech.*, 1934, **20**, 298A. H. Metzger, *Z. angew. Chem.*, 1930, **43**, 289; *Chem. Abs.*, 1930, **24**, 4621; *Brit. Chem. Abs.* **B**, 1930, 496. K. M. Watson, J. L. Wien and G. B. Murphy, *Ind. Eng. Chem.*, 1936, **28**, 605; *Brit. Chem. Abs.* **B**, 1936, 677; *J. Inst. Pet. Tech.*, 1936, **22**, 344A; *Chem. Abs.*, 1936, **30**, 4655.

[168] J. B. Hill and H. B. Coats, *Ind. Eng. Chem.*, 1928, **20**, 641; *Chem. Abs.*, 1928, **22**, 2834.

[169] W. B. McCluer and M. R. Fenske, *Ind. Eng. Chem.*, 1932, **24**, 1371; *Brit. Chem. Abs.* **B**, 1933, 137; *Chem. Abs.*, 1933, **27**, 834.

[170] See C. M. Larson and W. C. Schwaderer, *Nat. Petr. News*, 1932, **24** (2), 26, 30, 34; 1933, **25** (9), 25; *Chem. Abs.*, 1933, **27**, 4913. *Oil Gas J.*, 1934, **33** (5), 10; *J. Inst. Pet. Tech.*, 1934, **20**, 521A. See also C. S. Cragoe, *Proc. World Pet. Congr.*, 1933, **2**, 529; *J. Inst. Pet. Tech.*, 1934, **20**, 296A; *Chem. Abs.*, 1934, **28**, 4883; *Brit. Chem. Abs.* **B**, 1934, 992. C. Walther, *Proc. World Petr. Congr.*, 1933, **2**, 419; *Chem. Abs.*, 1934, **28**, 4890; *Brit. Chem. Abs.* **B**, 1934, 744; *J. Inst. Pet. Tech.*, 1934, **20**, 297A. W. B. McCluer and M. R. Fenske, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 389; *Chem. Abs.*, 1935, **29**, 326; *Brit. Chem. Abs.* **B**, 1935, 54.

[171] A.S.T.M. Designation D 97-33; A.S.A. No. Z11. 5-1933; A.P.I. No. 506-33 "A.S.T.M. Standards," American Society for Testing Materials, Philadelphia, Pa., 1933. See also B. H. Moerbeek and A. C. van Beest, *J. Inst. Pet. Tech.*, 1935, **21**, 155; *Brit. Chem. Abs.* **B**, 1935, 614, 888; *Chem. Abs.*, 1935, **29**, 4561. *Oil Gas J.*, 1935, **33**, No. 42, 33; *Chem. Abs.*, 1935, **29**, 3816; *Brit. Chem. Abs.* **B**, 1936, 51. J. G. Phillips, U. S. P. 1,916,071, June 27, 1933, to E. E. Greiner; *Brit. Chem. Abs.* **B**, 1934, 354. P. Woog, *Proc. World Petr. Congr.*, 1933, **2**, 412; *Chem. Abs.*, 1934, **28**, 4889; *J. Inst. Pet. Tech.*, 1934, **20**, 154A. P. Woog and J. Givaudon, *Rev. pétrolifère*,

Use of Specific Refraction and Specific Dispersion in Examination of Petroleum Fractions. Specific dispersion is defined as 10,000 times the difference between two specific refractions. That is, for refractive indexes for the C and G′ lines,[173] the specific dispersion, *D*, may be written:

$$D = \left(\frac{n_{G'} - 1}{d} - \frac{n_C - 1}{d}\right)10^4$$

where $n_{G'}$ and n_C are refractive indexes for G′ and C lines, respectively, and d is the specific gravity. By using molar refractives, as given by the Lorentz-Lorenz formula,[174] in place of the specific refractions used above, the specific dispersion is given by the equation:

$$D = \left(\frac{n_{G'}^2 - 1}{n_{G'}^2 + 2} \cdot \frac{1}{d} - \frac{n_C^2 - 1}{n_C^2 + 2} \cdot \frac{1}{d}\right)10^4$$

The advantage of this formula is that it is possible to calculate n by the use of atomic refractions. The values obtained in this way are usually fairly satisfactory for saturated compounds but not for aromatic or unsaturated hydrocarbons.[175] The first equation above may be written

$$D = (n_{G'} - n_C)10^4/d$$

By substituting experimentally determined values for n_C and $n_G{}'$ it is possible to obtain values of *D*. After treatment of a specimen to remove aromatic compounds *D* should be less than 158.[176]

Marder[177] has outlined a procedure for estimation of the relative amount of paraffin and naphthene hydrocarbons in an oil from which olefins and aromatics have been removed by sulphuric acid treatment. This method depends upon a knowledge of the specific refraction of the sample being tested and of paraffins and naphthenes which are known to lie within the boiling range of the specimen.

Vlugter, Waterman and van Westen[178] have shown that the composition of a

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1935, 1632; *Chem. Abs.*, 1936, **30**, 2356. P. Woog, J. Givaudon, R. Sigwalt and J. Lienhart, *Bull. soc. chim.*, 1935, (5) **3**, 269; *Chem. Abs.*, 1936, **30**, 3992. C. G. Verver. *Proc. World Petr. Congr.*, 1933, **2**, 417; *J. Inst. Pet. Tech.*, 1934, **20**, 295A; *Chem. Abs.*, 1934, **28**, 4889.

[172] O. Wesp, *Petroleum Z.*, 1934, **30**; *Motorenbetrieb v. Maschinen-Schmierung*, 1934, **7**, 6; *Brit. Chem. Abs.* **B**, 1934, 744; *Chem. Abs.*, 1934, **28**, 7506.

[173] These are two Fraunhofer lines due to hydrogen. C has a wave length of 6562.8 Ångstrom units and is in the visible red. G′ has a wave length of 4340 5 Ångstrom units and is in the visible blue.

[174] The Lorentz-Lorenz relation gives the molar refraction, *R*, in terms of the refractive index, *n*, the molecular weight, *M*, and the density, *d*:

$$R = \frac{(n^2 - 1)M}{(n^2 + 2)d}$$

See P. Debye, "Polar Molecules." The Chemical Catalog Co., Inc., New York, **1929**.

[175] *Cf.* F. Eisenlohr, *Z. physik. Chem.*, 1910, **75**, 585; *Chem. Abs.*, 1911, **5**, 1218; *J.C.S.*, 1911, **100** (2), 81; *Chem. Zentr.*, 1911, **1**, 624. See also T. J. N. van der Hulst, *Rec. trav. chim.*, 1935, **54**, 518; *Chem. Abs.*, 1935, **29**, 6117.

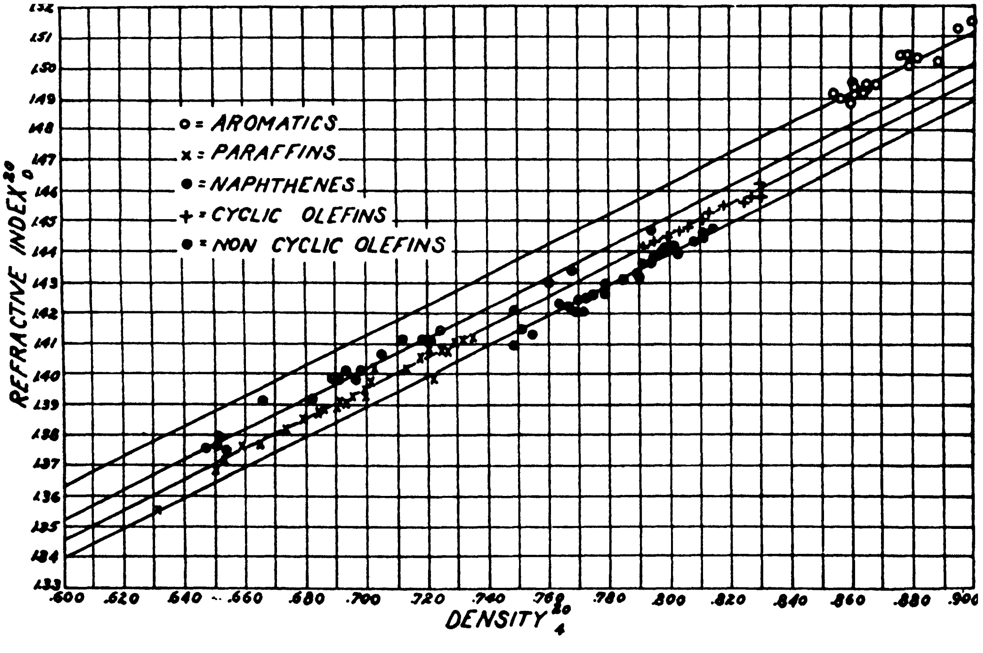
[176] J. C. Vlugter, H. I. Waterman and H. A. van Westen, *J. Inst. Pet. Tech.*, 1935, **21**, 701; *Chem. Abs.*, 1935, **29**, 7626; *Brit. Chem. Abs.* **B**, 1935, 934; *J. Inst. Pet. Tech.*, 1935, **21**, **367A**. See also E. Darmois, *Compt. rend.*, 1920, **171**, 952; *Chem. Abs.*, 1921, **15**, 622.

[177] M. Marder, *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 75, 222; *J. Inst. Pet. Tech.*, 1935, **21**, **162A**; *Chem. Abs.*, 1935, **29**, 8281.

[178] J. C. Vlugter, H. I. Waterman and H. A. van Westen, *J. Inst. Pet. Tech.*, 1935, **21**, 661; *Chem. Abs.*, 1935, **29**, 7057; *Brit. Chem. Abs.* **B**, 1935, 836; *J. Inst. Pet. Tech.*, 1935, **21**, **367A**. *Cf.* H. I. Waterman, J. J. Leendertse and G. van der Neut, *J. Inst. Pet. Tech.*, 1935, **21**, **816**; *Brit. Chem. Abs.* **B**, 1935, 980; *Chem. Abs.*, 1935, **29**, 8303. H. I. Waterman and J. J. Leendertse, *Rec. trav. chim.*, 1935, **54**, 725; *Chem. Abs.*, 1936, **30**, 2816; *Brit. Chem. Abs.* **A**, 1935, 1479. A. L. Ward and W. H. Fulweiler, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 396; *Brit. Chem. Abs.* **A**, **1935**, **61**.

high-boiling mixture of hydrocarbons may be most satisfactorily expressed as per cent each of aromatic rings, naphthenic rings and paraffin-side-chains. They showed that the composition could be calculated from a knowledge of the molecular weight, refractive index, density and aniline point of the oil. This was made possible in part by means of experimentally determined graphs and partly by calculations involving the known values.

A method for determining the various homologous series of light petroleum fractions has been advanced.[179] It depends upon the fact that for a given structural type of hydrocarbon, the refractive index varies linearly with the density. When these data are plotted, the equation which describes the relation is shown to be



Courtesy Industrial and Engineering Chemistry

FIG. 295.—Derivation of Refractivity Intercept for Hydrocarbons. (S. S. Kurtz, Jr., and C. E. Headington)

$$\text{Refractivity index} = 0.5 \text{ density} + b$$

where b is a constant which represents the refractive index at zero density. This value, called the refractivity intercept, is different for each homologous series, as may be seen from Fig. 295. Some of the refractivity intercepts are indicated in Table 213.

Examination of Petroleum Fractions by Means of Critical Solution Temperatures. The temperature at which an oil and a solvent liquid become completely miscible is known as the "critical solution temperature." Because of the different solubility of the several classes of hydrocarbons in solvents, such as

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[179] S. S. Kurtz, Jr., and C. E. Headington, *Ind. Eng. Chem., Anal. Ed.*, 1937, **9**, 21. S. S. Kurtz, Jr., and A. L. Ward, *J. Franklin Institute*, 1936, **222** (5), 563.

TABLE 213.—*Refractivity Intercepts of Hydrocarbons.*

Hydrocarbon Type	Refractivity Intercept
Paraffins	1.0461
Naphthenes	1.0400
Aromatics	1.0627
Cyclic monoölefins	1.0461
Noncyclic monoölefins	1.0521
Cyclic conjugated diolefins	1.0643
Noncyclic conjugated diolefins	1.0877
Noncyclic nonconjugated diolefins	1.0592

aniline, nitrobenzene or benzyl alcohol, it is possible to obtain an indication of the nature of an oil from its critical solution temperature in one of those solvents.[180] In determining the amount of naphthenes and paraffins in an oil after hydrogenation of aromatics and olefins, Vlugter, Waterman and van Westen[181] have used the aniline point as a means of indicating complete hydrogenation. According to Griffith and Hollings[182] the portion of oil which is insoluble in oleum is also least soluble in aniline. They also suggested that curves of aniline point versus boiling point gave some indication of the previous history of the oil. An oil which had undergone cracking treatment gave a flexed curve, whereas with a crude oil the graphic relation was linear.

Besides aniline, nitrobenzene and benzyl alcohol, several other organic liquids have been used in the study of critical solution temperature. A solution of 9 parts acetone and 1 part amyl acetate is recommended by Vellinger and Herrenschmidt[183] for highly refined oils. Nitromethane has been proposed as a medium for the identification of the types of hydrocarbons.[184] Thus, solid aromatic hydrocarbons are more soluble than other hydrocarbons of approximately the same melting point and molecular weight. In approximately increasing order of solubility in nitromethane at 20°C., the various hydrocarbons are: alkanes, cycloalkanes, dicycloalkanes, cycloalkenes, alkadienes containing more than eight carbon atoms, alkynes, alkenes and aromatics. The latter are much more soluble than any other type. The critical solution temperatures of various hydrocarbons in liquid sulphur dioxide and likewise in liquid ammonia have been determined as a possible means for the separation of isomers.[185] However, it appears that aniline holds more promise than either of the last-mentioned solvents.

The kauri-butanol test for solvent power may be considered as dependent upon critical solubility. It consists of ascertaining the volume (in cc.) of a solvent which will cause sufficient opacity, when added to 20 g. of standard kauri solution at 77°F., to make 10 point print illegible when viewed through the flask.[186] "The standard kauri solution is prepared by adding 100 g. of carefully selected kauri gum to 500 g. of *n*-butyl alcohol (distilling between 114.4 and 116.6°C.). The mixture is heated gently in a flask provided with a water-cooled reflux condenser, allowed to cool, and after 96 hours decanted into a clean, dry bottle always kept well stoppered." Higher-boiling butanol may be used. The test is carried out in a 250 cc. flat-bottomed flask, the solvent to be tested being run into the kauri-butanol solution in the flask until the end point is reached. Because of the variation in kauri gum from different sources, it is necessary to correct the kauri-butanol values to some standard. Benzene is used for this purpose, its kauri-butanol value being determined and known as the "benzene equivalent" of the kauri solution. To make final results comparable, the kauri-butanol value as determined is divided by the benzene equivalent of the solution and multiplied by 100. The kauri-butanol value is considered to be an indication of aromaticity of a solvent. It is recommended as an index of solvent power for hydrogenated petroleum solvents by Baldeschwieler and his co-workers. Aniline point has also been recommended as an index of solvent power in petroleum solvents to be used in paint formulation.[187]

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[180] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

[181] J. C. Vlugter, H. I. Waterman and H. A. van Westen, *J. Inst. Pet. Tech.*, 1935, **21**, 661; *Chem. Abs.*, 1935, **29**, 7057; *Brit. Chem. Abs.* **B**, 1935, 836. See also E. B. Evans, *J. Inst. Pet. Tech.*, 1937, **23**, 220, 208A.

[182] R. H. Griffith and H. Hollings, *J. Inst. Pet. Tech.*, 1933, **19**, 701; *Chem. Abs.*, 1933, **27**, 5523; *Brit. Chem. Abs.* **B**, 1933, 949. *Cf. J. Inst. Pet. Tech.*, 1934, **20**, 255.

[183] E. Vellinger and J. D. Herrenschmidt, *Compt. rend.*, 1935, **201**, 780; *Brit. Chem. Abs.* **B**, 1936, 83; *Chem. Abs.*, 1936, **30**, 274.

[184] S. P. Mulliken and R. L. Wakeman, *Rec. trav. chim.*, 1935, **54**, 366; *Chem. Abs.*, 1935, **29**, 3975; *J. Inst. Pet. Tech.*, 1935, **21**, 401A. See also *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 275; *Brit. Chem. Abs.* **B**, 1935, 837; *Chem. Abs.*, 1935, **29**, 5805; *J. Inst. Pet. Tech.*, 1935, **21**, 370A.

[185] R. T. Leslie, *J. Research Natl. Bur. Standards*, 1934, **13**, 589; *J. Inst. Pet. Tech.*, 1935, **21**, 87A; *Brit. Chem. Abs.* **A**, 1935, 159; *Chem. Abs.*, 1935, **29**, 987.

[186] E. L. Baldeschwieler, W. J. Troeller and M. D. Morgan, *Ind. Eng. Chem., Anal. Ed.*, 1935, **7**, 374.

Surface Tension and Parachor in the Analysis of Petroleum Fractions. Surface tension may be defined as the force at the surface between two fluids which is due to molecular attractions. Air is commonly taken as one phase. The surface tension, γ, may be measured by a rise, h, in a capillary radius, r, for a liquid of density, d, according to the formula:

$$\gamma = rhdg/2$$

The tension will be found in dynes per centimeter, if r and h are in cm., d in grams per cm.^{3} and g (the acceleration due to gravity) in cm. per sec.^{2}

Pfund and Greenfield[188] have proposed a method which is said to be especially practical for the determination of the surface tension of non-volatile, relatively viscous liquids. It depends upon the observation that if a jet of air is permitted to impinge upon the surface of a liquid, the depth of the depression produced is inversely proportional to the square of the surface tension. The depth of the depression is measured by the aid of a short-focus telescope with micrometer eye-piece. A calibration chart to facilitate the determinations is prepared by the use of substances of known surface tension.

A du Noüy tensimeter[189] has been used by Vellinger and Radulesco[190] to study the change of interfacial tension as measured against buffer solutions during refining of mineral oils. They demonstrated that the interfacial tension was higher for more highly refined oils.

The parachor of a substance is defined by the relationship:

$$P = M\gamma^{\frac{1}{4}}/(D - d)$$

where γ is the surface tension, M, the molecular weight and D and d are the densities of liquid and vapor phases, respectively.[191] The value of P, called the molecular parachor, may be calculated with a fair degree of accuracy from values for the different portions of the molecule such as carbon, hydrogen, nitrogen and the halogens. Some of the characteristic increments for parachor are given in Table 214.

The parachor represents a comparison of molecular volumes for liquids at temperatures at which they have the same surface tension. This constant, P, has been found to be useful in determining various properties of substances. For example, it is related to the octane rating of a gasoline (Chapter

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[187] E. M. Toby, Jr., *Am. Paint J.*, 1936, **20**, 7, 62, 64, 66; *Chem. Abs.*, 1936, **30**, 2407.

[188] A. H. Pfund and E. W. Greenfield, *Ind. Eng. Chem., Anal Ed.*, 1936, **8**, 81.

[189] A tensimeter which depends upon the force necessary to remove a platinum ring from the liquid interface. *Cf.* H. S. Taylor, "Treatise of Physical Chemistry," D. van Nostrand Co., New York, 1932, 1628. This is similar to the so-called "Jolly balance platinum ring method."

[190] E. Vellinger and G. Radulesco, *Ann. combustibles liquides*, 1934, **9**, 279; *Chem. Abs.*, 1934, **28**, 6285. *Proc. World Petr. Congr., London*, 1933, **2**, 407; *Brit. Chem. Abs.* B, 1934, 742; *Chem. Abs.*, 1934, **28**, 4889. See also E. Vellinger, *Compt. rend. congr. graissage*, 1931, 354; *Chem. Abs.*, 1933, **27**, 4913.

[191] S. Sugden, *J.C.S.*, 1924, **125**, 1177; *Chem. Abs.*, 1925, **19**, 197. S. Sugden and H. Wilkins *J.C.S.*, 1927, 139; *Chem. Abs.*, 1927, **21**, 1249.

TABLE 214.—*Values of Molecular Parachor.*

Group	Increment	Group	Increment
Carbon	4.8	Triple bond	46.6
Hydrogen	17.1	Double bond	23.2
Oxygen	20.0	Single bond	0
Nitrogen	12.5	Three-membered ring	17
Chlorine	54.3	Four-membered ring	11.6
Bromine	68.0	Five-membered ring	8.5
Iodine	91.0	Six-membered ring	6.1

44.) Marder[192] has applied the parachor to the determination of the composition of gasoline. He showed that it was possible to determine the extent of elimination of a certain type of hydrocarbon group, such as the removal of olefins or aromatics by sulphuric acid treatment. With unsaturated compounds it was possible to calculate the average number of double bonds per molecule and with aromatic compounds either the degree of hydrogenation for compounds of the lower members or the number of rings per molecule for compounds of higher boiling point. The average number of carbon atoms in naphthene rings can also be calculated.

RAMAN EFFECT IN PETROLEUM CHEMISTRY

Although the Raman effect did not receive very much attention from petroleum chemists during the first few years after its discovery, it has been suggested as a possible means of throwing light on various factors which are of interest in the study of petroleum fractions.[193]

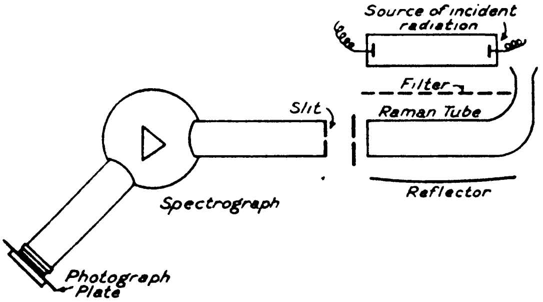

FIG. 296. Diagram of Experimental Arrangement for Recording Raman Spectra. (J. H. Hibben)

Courtesy Industrial and Engineering Chemistry
Courtesy Geophysical Laboratory, Carnegie Institution of Washington, D. C.

In 1928 Raman[194] reported his observations of a new radiation excited in glycerine by ultraviolet radiation. Landsberg and Mandelstam[195] observed the same effect in a quartz crystal at about the same time. This was considered to be the first experimental evidence of a phenomenon predicted earlier by Smekal.[196]

In the determination of the so-called Raman lines, or spectra, it is necessary to use light of a single wave length, as each wave length excites a different group of lines. One of the most satisfactory sources of monochromatic light is the mercury vapor lamp. For several reasons the lines of mercury at 4358 and 4047 Å are used as excitants, in which case it is unnecessary to employ a quartz optical system. A diagram of the apparatus is shown in Fig. 296. It is sometimes found helpful to insert a filter containing mercury vapor between the Raman tube and spectroscope, as this reabsorbs the lines due to the mercury and permits identification of lines close to the exciting frequency.

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[192] M. Marder, *Oel. Kohle, Erdoel, Teer,* 1935, **11**, 1, 41, 150, 182, 222; *Chem. Abs.*, 1935, **29**, 8281; *J. Inst. Pet. Tech.*, 1935, **21**, 126A, 159A; *Brit. Chem. Abs.* **B**, 1936, 1077; *Chem. Zentr.*, 1935, **2**, 1644. Also, specific parachor has been related to cetene numbers of gas oils. See D. J. W. Kreulen, *J. Inst. Pet. Tech.*, 1937, **23**, 253.

[193] J. H. Hibben, *Ind. Eng. Chem.*, 1934, **26**, 646; *Brit. Chem. Abs.* **B**, 1934, 662; *Chem. Abs.*, 1934, **28**, 4311; *J. Inst. Pet. Tech.*, 1934, **20**, 483A. Because of the voluminous literature on all phases of the Raman effect, it is impossible to give here more than a few of the essential features.

[194] C. V. Raman, *Indian J. Physics*, 1928, **2**, 387; *Chem. Abs.*, 1928, **22**, 2707.

[195] G. Landsberg and L. Mandelstam, *Naturwissenschaften*, 1928, **16**, 557; *Chem. Abs.*, 1928, **22**, 3837.

[196] A. Smekal, *Naturwissenschaften*, 1923, **11**, 873; *Chem. Abs.*, 1924, **18**, 2834. *Naturwissenschaften*, 1928, **16**, 612; *Chem. Abs.*, 1928, **22**, 3836.

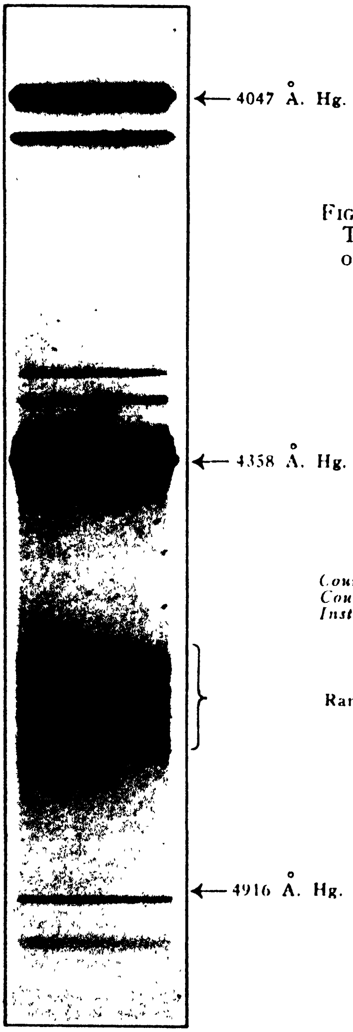

Fig. 297.
Typical Unfiltered Raman Spectrum of Cracked Gasoline. (J. H. Hibben)

Courtesy Industrial and Engineering Chemistry
Courtesy Geophysical Laboratory, Carnegie Institution of Washington, D. C.

The cause of the Raman effect is the loss of energy by quanta of light when they rebound from the molecules of the substance in the Raman tube.[197] Thus, a quantum with the energy hν (where h is Planck's constant and ν is the frequency of the incident light) is absorbed by a molecule and immediately re-emitted with a new frequency ν_1. The energy of the emitted quantum is measured by $h\nu_1$. If energy is given up to the molecule, that is, if $\nu_1 < \nu$, the emitted light will have a longer wave length. The spectral lines which are observed as a result of this are known as Stokes lines. In the opposite case, i.e., if the molecule is in an excited state and gives up energy, the emitted light has a shorter wave length. The spectral lines caused by this are anti-Stokes lines.

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[197] For a discussion of the mathematics and theoretical aspects of this phenomenon, see G. B. B. M. Sutherland, "Infra-Red and Raman Spectra," Methuen & Co. Ltd., London, 1935.

It has been found that there are certain frequencies of vibration which are more or less characteristic of any particular linkage in a molecule. This frequency is taken up by the molecule when a quantum is absorbed and re-emitted. Consequently the difference $\nu - \nu_1$ is some indication of the nature of the molecule from which the quantum was emitted. It is apparent that this difference should be unaffected by the value of ν, and consequently it is customary to speak of Raman shifts as $\Delta\nu$ expressed in wave numbers per centimeter, i.e., the frequency difference $\nu - \nu_1$.

Although $\Delta\nu$ is more or less characteristic for any particular grouping such as the C-H bond, the nature of the remainder of the molecule has some influence on the frequency of oscillation of the molecule and hence on $\Delta\nu$. A few of the characteristic values for $\Delta\nu$ are shown in Table 215.[198]

TABLE 215.—*Wave Shifts Characteristic of Certain Organic Groupings.*

Bond	($cm.^{-1}$)	Bond	($cm.^{-1}$)
C—H (aliphatic)	2930	C=O	1640 to 1730
C—H (aromatic)	3050	C≡N	2200
C=C	1600	NO_2	1400
C≡C	1960	CH_2	1440

Hibben[199] has suggested that the Raman effect may be of use in study of peroxidation and other phenomena which are of interest in petroleum chemistry. He observed, for example, that aluminum chloride modifies the Raman spectra of a solvent in which it is dissolved. It was believed that this might possibly give some indication of the catalytic effect of aluminum chloride on polymerization. It has also been possible to indicate the nature of the polymerization of compounds such as aldehydes and styrene.[200]

The study of complex mixtures by means of Raman spectroscopy is still rather limited. The presence of as little as 1 per cent of ethylenic substances in cyclopropane has been demonstrated by means of Raman spectra.[201] Although the existence of double bonds in cracked gasoline can be shown more readily by other methods, it is interesting to see that Raman spectra show their presence. In Fig. 297 is shown the Raman spectrum obtained for cracked gasoline, and in Fig. 298 a microphotometer tracing of the spectogram.[202] Some of the lines which could be associated with certain groups have been indicated on the latter figure.

TESTING OF KEROSENE

Many of the tests which have been mentioned heretofore are applicable to kerosene, such as color, sulphur and distillation tests. Also, there are some which are applicable almost solely to kerosene.[203] One of the most important is the "tendency to smoke test," which depends on the aromatic and naphthene content of the oil. The presence of certain amounts of these compounds is desirable as they give to the kerosene some of its useful illuminating properties.[204] The optimum amount is said to be from 10 to 20 per cent, since higher proportions may cause excessive smoking during burning.

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[198] A. Dadieu and K. W. F. Kohlrausch, *Ber.*, 1930, **63**, 251; *Chem. Abs.*, 1930, **24**, 2051; *Brit. Chem. Abs.* **A**, 1930, 663.

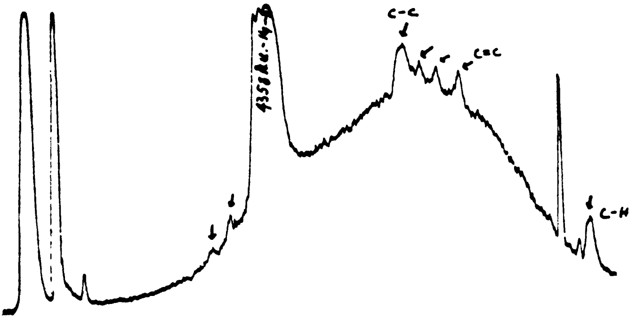
[199] J. H. Hibben, *loc. cit.*

[200] S. Venkateswaran and S. Bhagavantam, *Proc. Roy. Soc.* (*London*), 1930, **128A**, 252; *Chem. Abs.*, 1930, **24**, 5627; *Brit. Chem. Abs.* **A**, 1930, 1090. J. H. Hibben, *J.A.C.S.*, 1931, **53**, 2418; *Brit. Chem. Abs.* **A**, 1931, 893; *Chem. Abs.*, 1931, **25**, 3568. R. Signer and J. Weiler, *Helv. Chim. Acta*, 1932, **15**, 649; *Chem. Abs.*, 1932, **26**, 5497; *Brit. Chem. Abs.* **A**, 1932, 559.

[201] R. Lespieau, M. Bourquel and R. Wakeman, *Compt. rend.*, 1931, **193**, 1087; *Bull. soc. chim.*, 1932, **51**, 400; *Chem. Abs.*, 1932, **26**, 2655, 3992; *Brit. Chem. Abs.* **A**, 1932, 109, 675.

[202] J. H. Hibben, *loc. cit*

The tendency to smoke is measured as the maximum height of non-smoking flame obtainable on burning the kerosene in an especially designed apparatus.[205] Terry and Field[206] have designed a lamp for smoke point the results in which are stated to be reproducible to within 0.10 inch flame height or better. A porcelain dish on which smoke is to collect is cooled by cracked ice. The lamp consists of a brass fount with approximately 4-ounce capacity, wick tube ¼ in. diameter, wick therefor, a brass screen to permit access of air to the flame, a chimney made of 7 in. of 1-in. tubing and a scale of aluminum mounted at the side of the burner. A flame height of approximately 1, 2 or 3 inches characterizes an inferior, well refined or highly refined kerosene, respectively. The test, which consists of turning up the flame until it just smokes, can be completed in about 20 minutes.



Courtesy Industrial and Engineering Chemistry
Courtesy Geophysical Laboratory, Carnegie Institution of Washington, D. C.

FIG. 298.—Microphotometer Tracing of Raman Spectrum of Cracked Gasoline. (J. H. Hibben)

TESTING OF BLENDED MIXED FUELS

In Chapter 44 it was shown that many blended fuels tend to separate in two phases due to the absorption of water. The analysis of the motor fuel to ascertain the relative amounts of gasoline, alcohol and benzene is necessary as this relationship determines to a considerable extent the separating tendency of the product.

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[203] See A. N. Sakhanov, *Neft. Khoz.*, 1926, 11, 233; *Chem. Abs.*, 1928, **22**, 3286. R. Stansfield and A. R. Stark, *Proc. World Petr. Congr., London*, 1933, **2**, 706; *Chem. Abs.*, 1934, **28**, 4883; *Brit. Chem. Abs.* **B**, 1934, 743.

[204] See, for example, B. H. Moerbeek, *Proc. World Petr. Congr., London*, 1933, **2**, 713; *J. Inst. Pet. Tech.*, 1934, **20**, 169A; *Chem. Abs.*, 1934, **28**, 4883; *Brit. Chem. Abs.* **B**, 1934, 743. W. Jakobowicz, *Przemysl. Naftowy*, 1933, **8**, 284; *Chem. Abs.*, 1933, **27**, 4064.

[205] For the earlier development of these methods, see: J. Kewley and J. S. Jackson, *J. Inst. Pet. Tech.*, 1927, **13**, 364; *Chem. Abs.*, 1927, **21**, 4057. C. L. Gilbert, *Proc. World Petr. Congr., London*, 1933, **2**, 735; *Chem. Abs.*, 1934, **28**, 4885; *J. Inst. Pet. Tech.*, 1934, **20**, 244A; *Brit. Chem. Abs.* **B**, 1934, 743. W. H. Thomas, *J. Inst. Pet. Tech.*, 1927, **13**, 402; *Chem. Abs.*, 1927, **21**, 4057. S. Bowman, *ibid.*, 410; *Chem. Abs.*, 1927, **21**, 1178. W. A. Woodrow, *Proc. World Petr. Congr., London*, 1933, **2**, 732; *J. Inst. Pet. Tech.*, 1934, **20**, 244A; *Chem. Abs.*, 1934, **28**, 4885; *Brit. Chem. Abs.* **B**, 1934, 820. B. H. Moerbeek, *ibid.*, 730; *J. Inst. Pet. Tech.*, 1934, **20**, 170A; *Chem. Abs.*, 1934, **28**, 4885; *Brit. Chem. Abs.* **B**, 1934, 743. S. T. Minchin, *ibid.*, 738; *Chem. Abs.*, 1934, **28**, 4885; *J. Inst. Pet. Tech.*, 1934, **20**, 170A; *Brit. Chem. Abs.* **B**, 1934, 867. J. S. Jackson, *ibid.*, 699; *Brit. Chem. Abs.* **B**, 1934, 743; *Chem. Abs.*, 1934, **28**, 4883.

[206] J. B. Terry and E. Field, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 293; *Chem. Abs.*, 1936, **30**, 6177; *J. Inst. Pet. Tech.*, 1936, **22**, 498A.

A method for the estimation of alcohol in blends with gasoline fractions is extraction of a known volume of sample with 5 volume per cent water followed by measurement of the volume of water layer. Reference to experimentally determined tables made it possible to estimate the original composition.[207] Lampe has suggested[208] determining the density of the benzine portion after separation from alcohol either by treatment with water or, better, an aqueous solution of calcium chloride. If the value is from 0.87 to 0.88, it indicates that the hydrocarbon layer consists of benzene. If only gasoline is present, its specific gravity can be determined from the composition and density of the original mixture.[209]

Herbrich[210] has outlined a method for determining the critical amount of water which will cause separation at 0°C. The procedure is similar to other methods which depend on critical solution temperature.

In determining the amount of alcohol in blends which contain benzene, it is hardly sufficient to add water alone, as there is some tendency for benzene to retain alcohol and vice versa. By using dilute sulphuric acid, which combines with alcohol, Spausta[211] found that it is possible to get complete separation. It is also said to be feasible to isolate certain hydrocarbons for subsequent study. As a suggested color reaction, the addition of specific dyes, algol red B or lacquer red Ciba B, to an alcohol-blended fuel in which there is benzene is said to give a rose or red solution.[212]

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[207] See W. R. Ormandy, T. W. M. Pond and W. R. Davies, *J. Inst. Pet. Tech.*, 1934, **20**, 913; *Brit. Chem. Abs.* **B**, 1934, 1047; *Chem. Abs.*, 1934, **28**, 4862.

[208] B. Lampe, *Z. Spiritusind.*, 1934, **57**, 252, 254; *Chem. Abs.*, 1935, **29**, 3453; *Brit. Chem. Abs.* **B**, 1934, 996

[209] A graphic method for the determination of the specific gravity of motor-fuel mixtures is given by R. Hase, *Automobiltech. Z.*, 1934, **37**, 574, *Chem. Abs.*, 1935, **29**, 3133

[210] J. Herbrich, *Ann. combustibles liquides*, 1933, **8**, 1113; *Brit. Chem. Abs.* **B**, 1934, 1047; *Chem. Abs.*, 1934, **28**, 1501.

[211] F. Spausta, *Mitt. tech. Versuchtsamtes, Wien*, 1933, **22**, 9; *Chem. Abs.*, 1934, **28**, 4201.

[212] J. Formanek, *Chem. Obzor*, 1934, **9**, 41; *Chem. Abs.*, 1934, **28**, 5627; *Brit. Chem. Abs.* **B** 1935, 536.

Chapter 51

Petroleum Asphalts

Petroleum asphalts are the thick viscous residues obtained by distillation (or cracking) operations, as well as by oxidizing or sulphurizing high-boiling fractions. The proportion of asphaltic (and resinous) substances found in crude petroleums are generally greater the higher the specific gravity and sulphur content of the oil. The data for some American oils are given by Sommer,[1] in Table 216.

TABLE 216.—*Asphalt Content of Various Crude Oils.*

Crude Oil	Sp. Gr.	% Sulphur	% Hard Asphalt
Texas	0.8955	0.33	0.10
Mexican	0.930	3.27	11.08
Californian	0.944	3.3	14.98
Venezuelan	0.980	7.89	17.0

The components of asphalt are usually considered to be oily materials, resins, asphaltenes, carbenes and carboids, complex bodies which probably represent a series of increasingly polymerized or condensed cyclic hydrocarbons.[2] The close resemblance of petroleum and natural asphalts both in composition and in applicability is pointed out by Marcusson.[3] In general, natural asphalts show a relatively high proportion of mineral constituents whereas petroleum asphalts contain less than 1 per cent. Furthermore, free asphaltogenic acids are present in the latter only in small quantities, if at all. Petroleum asphalts, on the other hand, contain a much larger proportion of oily constituents, often 40 to 80 per cent. The consistency of the latter, however, varies considerably, depending upon the source of the asphalt and its subsequent treatment.

In this chapter discussion will be limited to the preparation, properties and uses of petroleum asphalt, that is, those materials obtained in the refining of various petroleum distillates or residues, or by treatment of the latter as, for example, by oxidation.

OILY CONSTITUENTS

These have been described as thick, fluorescent oils, consisting of unsaturated and saturated hydrocarbons, the latter being probably mainly naphthenes or polynaphthenes.[4] Mack[5] considers that these oily bodies form an essential part of asphalts and influence to a high degree the properties of the latter substances. He found that asphaltenes swelled on being heated in contact with oils derived from asphalts of high susceptibility (*q.v.*) to temperature changes. On continued heating, solution was effected. However, the oleaginous liquids, except those containing a high proportion of sulphur compounds, from asphalts of low susceptibility were non-solvents for asphaltenes. The physical properties of oils from several different asphalts are given in Table 217. Those liquids having a high viscosity-gravity constant,[5a] specific gravities and refractive indices (indicating the presence of cyclic hydrocarbons) were good solvents for asphaltenes. Those oils (particularly samples B and C) for which these values were low were poor solvents.

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[1] A. Sommer, *Petroleum*, 1915, 11, 151.

[2] J. Marcusson, *Z. angew. Chem.*, 1919, **32**, 113; *Chem. Abs.*, 1919, **13**, 2592.

[3] J. Marcusson, *Z. angew. Chem.*, 1918, **31**, 113, 119; *J.S.C.I.*, 1918, **37**, 403A.

[4] P. E. Spielmann, "Bituminous Substances," Ernest Benn, Ltd., London, 1925.

[5] C. Mack, "Physico-Chemical Aspects of Asphalts," Proceedings of the Technical Session of the Association of Asphalt Paving Technologists, Dec., 1933.

TABLE 217.—*Characteristics of Oily Constituents.*

Sample	Sulphur Content	Sp. gr. at 60°F.	Visc. at 210°F. (Saybolt)	Visc.-Grav. Constant	Index of Refraction
A	5.2%	0.9883	510 sec.	0.927	1.5410
B	—	0.9541	745 "	0.862	1.5128
C	—	0.9544	977 "	0.859	1.5275
D	—	0.9814	660 "	0.900	1.5405
E	—	0.9944	560 "	0.920	1.5450
F	—	1.0396	340 "	0.986	1.584

One procedure for isolating the oily portion of asphalts comprises treatment of the specimen with 88°Bé. straight-run naphtha, filtering the insoluble material, and evaporating the naphtha from the filtrate.[6] The non-volatile liquids thus obtained are absorbed by about five times their weight of fuller's earth and the latter then extracted with the naphtha. Evaporation of the solvent yields the oily constituents.

It is interesting to note that stable, water-white hydrocarbons have been prepared from Trinidad asphalt.[7] The procedure consisted in treating the asphalt with petroleum ether (boiling below 50°C.) thus effecting separation into soluble petrolene hydrocarbons and insoluble asphaltenes. The latter were removed by filtration and the solution then subjected to the action of fuller's earth to eliminate resinous materials. Petrolene hydrocarbons were recovered by vacuum evaporation of the solvent. The extract thus obtained was dark olive green in color. This was then distilled (at pressure less than 1 mm.) and two fractions taken over, one boiling at —69 to 135°C. and the other at 135 to 185°C. The undistilled residue was almost solid at room temperature.

The lower boiling fraction was treated repeatedly with an equal volume of 98 per cent sulphuric acid until the acid layer had only a pale red color. The oil layer was then washed with water, dehydrated over metallic sodium, and redistilled *in vacuo*. A water-white distillate was secured. The higher-boiling fraction, after dilution with petroleum ether (previously acid-treated) was subjected to the action of sulphuric acid, washed with water, dried over sodium, and the ether evaporated under reduced pressure. Distillation *in vacuo* of this refined fraction yielded a water-white, nonfluorescent distillate.

The third fraction, or undistilled residue, also was diluted with petroleum ether, washed successively with sulphuric acid and water, freed from solvent, dried and distilled (*in vacuo*) to a boiling point of 263°C. During acid treatment in this instance a tarry layer separated. The latter, after refining as outlined, also yielded a water-white distillate.

[5a] This is given by the relation

$$A = \frac{G - 0.24 - 0.022 \log(V - 35.5)}{0.755}$$

in which A is the constant, G the specific gravity at 60°F. and V the viscosity in seconds (Saybolt) at 210°F. For a discussion of this constant see J. B. Hill and H. B. Coats, *Ind. Eng. Chem.*, 1928, 20, 641.

[6] R. R. Thurston and F. C. Knowles, *Ind. Eng. Chem.*, 1936, **28**, 88; *Chem. Abs.*, 1936, **30**, 2739; *Brit. Chem. Abs.* **B**, 1936, 306.

[7] H. T. Gaetz, *Ind. Eng. Chem.*, 1935, **27**, 647; *Chem. Abs.*, 1935, **29**, 5258; *Brit. Chem. Abs.* **B**, 1935, 709; *J. Inst. Pet. Tech.*, 1935, **21**, 308A.

RESINS

The chemical properties and structures of the resinous and asphaltic constituents of petroleum are imperfectly known and their separation from oils is accomplished by empirical methods based on their insolubility in various solvents. According to Holde and Eickmann[7a] four types of substances may be obtained:

(1) Hard asphalt by precipitation with benzine (sp.gr. 0.70). From sulphur-containing oils this appears to be a variety of asphaltum.
(2) Softer asphalt by the use of an alcohol-ethel mixture. The proportion of insoluble material is greater with this solvent than with benzine.
(3) Amyl alcohol precipitates not only the same materials as alcohol-ether mixture, but in addition a large amount of resinous materials. This solvent has been proposed for the preparation of lubricating oils free of asphaltic and resinous materials.[8]
(4) Extraction of resinous materials with 70 per cent alcohol.

The resinous materials obtained from a machine oil distillate with the last-named solvent had oxygen contents greater than the original oil, gravity was greater than 1 and iodine number of 15 to 26 as compared with 7.6 for the oil.[9] Furthermore, they contained 11.8 per cent of saponifiable constituents. Other solvents which may be employed for the extraction of such resins, particularly from lubricating or turbine oil distillates, are acetone or castor oil,[10] or a mixture of methyl alcohol and a hydroaromatic hydrocarbon, e.g., cyclohexane.[11]

Adsorption agents, for example animal charcoal or Florida earth, may be substituted for solvents.[12] As an illustration, mazout is treated with bone charcoal, which is freed afterwards from oil by washing with benzine, and then extracted successively with 70 per cent ethyl alcohol, amyl alcohol, ether, benzene and chloroform. In this manner partial fractionation of the resins was effected as indicated by the density, iodine number, sulphur content and molecular weights (given in Table 218) of the extracts.

TABLE 218. —*Characteristics of Resins from Mazout.*

Solvent	*d*	Extract Iodine Number	% Sulphur	Molecular Weight
Ethyl alcohol	1.0867	8.06	0.55	1588
Amyl alcohol . . .	1.059	16.23	1 02	1261
Ether.	1.044	32 31	2.11	801
Benzene	1 110	- -		-
Chloroform	1.077	-	-	

According to Vasiliev and Zhirnova,[13] silica gel is a much better adsorption agent than fuller's earth as the latter extracts only about 20 per cent as much resin and also effects polymerization.[14] After removal of asphaltogenic acids (with caustic soda) and asphaltenes (with benzine), these investigators treated petroleum distillates with silica gel at 50°C. The gel was then freed from oil with benzene, and the resins extracted with chloroform or a mixture of benzene and ethyl alcohol. The neutral products obtained in this manner exhibited molecular weights (in benzene) varying from 290 to 788, as compared with 5000-6000 for asphaltenes. The formulas of the resins appeared to be $C_nH_{2n-m}O_2$ in which n ranged from 16 to 69 and m from 8 to 48. This suggested that the compounds possessed a highly polycyclic structure which was only slightly unsaturated. The resins were easily converted to asphaltenes by oxidation which resulted in the removal of hydrogen and further condensation. Treatment with sulphuric acid yielded asphaltenes and sulphonated bodies.

[7a] D. Holde and R. Eickmann, *Petroleum*, 1907, **24**, 1077; *Chem. Abs.*, 1908, **2**, 1341.

[8] C. Daeschner, British P. 10,633, 1901; *J.S.C.I.*, 1902, **21**, 765; *Rev. prod. chim.*, **4** (20), 309; *J.S.C.I.*, 1902, **21**, 168.

[9] D. Holde and R. Eickmann, *Mitth. kgl. Materialprüfungsamt*, 1907, **25**, 8; *Chem. Abs.*, 1908, **2**, 177.

[10] F. Schwartz and J. Marcusson, *Z. angew. Chem.*, 1913, **26**, 385; *Chem. Abs.*, 1913, **7**, 3019.

[11] C. Krauch, M. Pier and A. Eisenhut, U. S. P. 1,960,974, May 29, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 4587.

[12] D. Holde and R. Eickmann, *loc. cit.* P. Smirnov, *Neft. Slantsevoe Khoz.*, 1925, **8**, 286; *J.S.C.I.*, 1925, **44**, 836B; *Chem. Zentr.*, 1925, **2**, 1000.

[13] N. A. Vasiliev and L. V. Zhirnova, *Neft. Khoz.*, 1929, **17**, 707; *Chem. Abs.*, 1930, **24**, 2869. See also, A. Sachanen and N. Vasiliev, *Petroleum Z.*, 1927, **23**, 1618; *Brit. Chem. Abs.* **B**, 1928, **78**.

[14] For a discussion of the action of various natural and treated earths on bitumen see H. T. Lorne, *J. Inst. Pet. Tech.*, 1936, **22**, 541; *Chem. Abs.*, 1936, **30**, 7831; *Brit. Chem. Abs.* **B**, 1936, 966.

In connection with the polycyclic nature of resins, it is interesting to note that extraction with benzine of the orange-colored, resinous, oily residue from the distillation of crude petroleum yielded a yellow crystalline hydrocarbon.[15] This hydrocarbon exhibited a spectrum similar to that of anthracene, had a specific gravity of 1.204, and melted at 420-430°C. Heated to higher temperatures it sublimed and distilled, giving off brilliant yellow fumes. It was designated petrozcene to indicate its polycyclic structure.

Resin-like bodies formed during the distillation of petroleum were examined by Siebeneck.[16] He reported that these distil over at 400°C. with steam in about a 0.3 per cent yield on the crude oil, have specific gravities greater than 1, softening points of about 45°C. and flow points about 60°C. They are partially soluble in benzine but completely so in benzene or other aromatic hydrocarbon solvents. The crude materials may be fractionated by steam distillation to give products of somewhat higher softening and flow points. Subjected to cracking distillation they yield paraffin oil and coke.

The resinous components of lubricating oils, although present to only a few tenths of a per cent, are solid, oxygenated, lac-like bodies.[17] Removal of these by an alcohol-ether mixture appears to reduce the gumming tendency of the lubricants. A method of preparing resins of petroleum origin comprises distillation of heavy, residual hydrocarbons at low pressures, to remove oily constituents, and extraction with a hydrocarbon solvent, e.g., naphtha or kerosene, to eliminate asphaltenes.[18] Aqueous suspensions of such resins are suggested as sizing agents for paper, for impregnation of porous paper and for the manufacture of laminated paper and board.[18a] Since these resinous bodies appear to be composed only of hydrocarbons, emulsions or suspensions of them may be prepared with the aid of bentonite, sodium salts of petroleum sulphonic acids, or the sodium soaps of acids made by oxidation of paraffin wax.[19] Another application of these resins includes their incorporation with rubber, rubber latex, chicle, gutta-percha or balata to form a chewing gum base.[19a]

ASPHALTENES

These compounds are found in crude petroleum and its distillates, particularly the higher-boiling fractions and residuums, and are probably the result of condensation and polymerization of the aromatic constituents in the oil. The asphaltene content of such oils varies over a wide range, being 0.25 per cent in Grozny paraffin-free petroleum to 32.3 per cent in solid petroleum pitch.[20] Analysis of asphaltenes from one oil showed a content of 85.5 per cent carbon, 6.8 per cent hydrogen and 7.7 per cent oxygen and sulphur. Air-blowing of a tar oil at 350°C. did not alter the composition or properties of the asphaltenes though it did increase their proportion from 13.7 to 32.3 per cent. Similarly, oxidation of (Weitzer) crude oil at 120-130°C. resulted in the conversion of resins into these more complex bodies.[21] Reaction in this instance was not accelerated by manganese dioxide or fuller's earth, as these catalysts were probably poisoned by sulphur compounds. According to Rogers and Shoemaker,[22] oxidation tests for the stability of lubricating oils are a measure of the time required (under specified conditions) for the rapid formation of asphaltenes. Compounds having compositions corresponding to 71.6 per cent carbon, 6.3 per cent hydrogen, 13.3 per cent oxygen and 8.1 per cent sulphur have been prepared by heating paraffins and naphthenes with sulphur and oxidizing with air.[23]

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[15] H. C. Tweedle, U. S. P. 189,402, Apr. 10, 1887.

[16] H. Siebeneck, *Petroleum Z.*, 1923, **19**, 939; *Chem. Abs.*, 1924, **18**, 462.

[17] A. E. Dunstan and F. B. Thole, *Chem. Met. Eng.*, 1923, **28**, 299. A. Seton, *J.S.C.I.*, 1929, **48**, 81.

[18] French P. 744,169, 1933, to Standard Oil Development Co.; *Chem. Abs.*, 1933, **27**, 4109. See also, S. C. Fulton, U. S. P. 2,055,486, Sept. 29, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 7842.

[18a] Carleton Ellis, U. S. P. 1,948,442, Feb. 20, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1934, **28**, 2906.

[19] Carleton Ellis, U. S. P. 2,042,299, May 26, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 4954.

[19a] Carleton Ellis, U. S. P. 1,976,774, Oct. 16, 1934, to Standard Oil Development Co.

With respect to the composition of asphaltenes, it is interesting to note that Nellensteyn[24] reports the following analysis of such bodies derived from asphaltic material (from Mohenjo-Daro) thought to be 5000 years old: carbon 78.2 to 78.7 per cent, sulphur 7.1 to 7.4 per cent, hydrogen 3 to 7.7 per cent, nitrogen 0.7 to 1.2 per cent, and oxygen 0.68 to 1.7 per cent.

According to Sakhanov,[25] asphaltenes are soluble in aromatic hydrocarbons, carbon disulphide,[25a] chloroform and carbon tetrachloride, and dissolution is accompanied by evolution of heat and by swelling whereby they are changed from hard, brittle particles to viscous, tough masses. The latter are highly dispersed colloidal solutions, and are as stable as aqueous gelatin solutions. Asphaltenes are lyophilic with respect to aromatic or halogenated hydrocarbons, carbon disulphide and petroleum tars, but lyophobic in relation to paraffins and naphthenes. Natural asphalts and petroleum pitch are probably solutions of asphaltenes in resins and heavy oils.

Chernozhukov[26] concluded from his experiments that the presence of sulphur compounds in oils during oxidation is essential for the formation of asphaltenes. Treatment of liquid paraffin with oxygen under 15 atmospheres pressure for 4 hours at 150°C. or with oxygen under 12 atmospheres pressure for 2 hours at 250°C. yielded on dilution with petroleum ether either a white precipitate or a light yellow flaky sediment, respectively. No asphaltenes or carbenes were noted in either case. On the other hand sulphur-containing distillates (turbine and spindle oils) from Balakhanui, Grozny or Emba crudes yielded asphaltenes having compositions corresponding to $C_{172}H_{176}O_{14}S$ and $C_{130}H_{142}O_{12}S$. Also white oils, after heating with sulphur, oxidizing under pressure and dilution with petroleum ether, gave insoluble bodies. When these were heated to 100°C. they furnished asphalt-like bodies apparently having the formula $(C_{24}H_{27}O_3S)_x$. It has been reported also that the resinous deposits obtained from Boryslaw (Galicia) paraffin oil, on storage, had a sulphur content of 2.5 per cent whereas the oils had only 0.1 per cent sulphur.[27]

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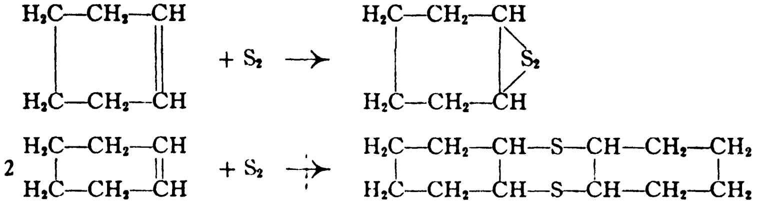
[20] A. N. Sakhanov, *Neft. Slantsevoe Khoz.*, 1924, 7, 933; *Chem. Abs.*, 1925, **19**, 3158.
[21] J. Marcusson and M. Picard, *Chem.-Ztg.*, 1924, **48**, 338; *J.S.C.I.*, 1924, **43**, 624B.
[22] T. H. Rogers and B. H. Shoemaker, *Ind. Eng. Chem., Anal. Ed.*, 1934, **6**, 419.
[23] V. Kalichevsky and S. C. Fulton, *Nat. Pet. News*, 1931, **23** (51), 33.
[24] F. J. Nellensteyn, *Chem. Weekblad*, 1934, **31**, 543; *Chem. Abs.*, 1935, **29**, 916.
[25] A. Sakhanov, *Petroleum Z.*, 1925, **31**, 1441; *J.S.C.I.*, 1925, **44**, 745B.
[25a] A discussion of methods for removal of carbon disulphide in recovering bitumens from solutions of the latter in this solvent is given by L. J. Chalk, *J.S.C.I.*, 1937, **56**, 156T.
[26] N. I. Chernozhukov, *Neft. Khoz.*, 1928, **15**, 670; *Chem. Abs.*, 1929, **23**, 1258.
[27] S. von Pilat and J. Dukiet, *Erdöl u. Teer*, 1926, **2**, 571; *Chem. Abs.*, 1926, **20**, 3560.

Spielmann[28] points out that since asphaltenes and resins are considered to be polycyclic bodies containing sulphur or oxygen, and both of these elements can exist in ring formations, such compounds may result from reactions indicated by



Asphaltenes react with sulphuric, or fuming sulphuric, acid to give oxonium compounds,[29] which are insoluble in water, unattacked by alkalies, but hydrolyzed (to sulphuric acid) by dilute hydrochloric acid.[30] With fuming nitric acid cyclic nitrogen derivatives (containing 4 to 6 per cent nitrogen) are obtained, which may be precipitated from an acetone solution by mercuric bromide or ferric chloride dissolved in ether. Alkalies transform them into water-soluble salts of isomeric isonitric acids.[31] The unsaturated character of asphaltenes is indicated by their reaction with halogens or halogen acids to give addition products. Also with chlorosulphonic acid they yield compounds containing both sulphur and chlorine. Oxidation with Caro's acid (monopersulphuric acid, H_2SO_5) of asphaltenes high in sulphur gives rise to sulphoxides and sulphones, while oxygen-containing compounds are produced from those low in sulphur. Nametkin and Putzillo,[32] however, report that perbenzoic acid reacts with asphaltenes but iodine does not.

As previously mentioned, benzine is employed for the precipitation of asphaltenes from petroleum distillates.[33] When this precipitant is used as an analytical reagent the following specifications are advocated for it:[34] d^{15} 0.695-0.705, a boiling range of 65-95°C., and not more than 2 per cent should be soluble in a

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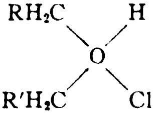
[28] P. E. Spielmann, "Bituminous Substances," Ernest Benn Ltd., London, 1925.

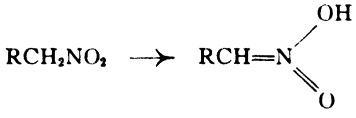
[29] Oxonium compounds are those in which an oxygen atom appears to function as a tetravalent element, e.g.,



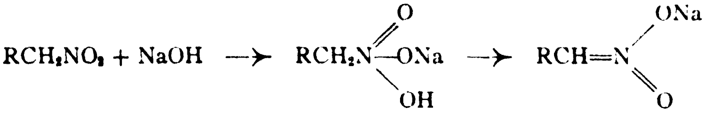
Numerous oxygen-containing substances, such as ethers, esters, ketones and aldehydes, exhibit this property.

[30] J. Marcusson, *Z. angew. chem.*, 1919, **32**, 113; *Chem. Abs.*, 1919, **13**, 2592.

[31] This transformation of nitro compounds is often indicated as



In the presence of alkali the reaction is sometimes represented by



[32] S. S. Nametkin and V. G. Putzillo. *Neft. Khoz.*, 1929, **16**, 230; *Brit. Chem. Abs.* **B**, 1930, 130.

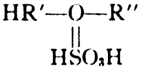
[33] For the refining of residues from asphaltic crudes with a solvent of this type, see O. E. Bransky and F. M. Rogers, U. S. P. 1,698,471, Jan. 8, 1929, to Standard Oil Co. of Indiana; *Chem. Abs.*, 1929, **23**, 1261.

[34] D. Holde and R. Eickmann, *loc. cit.* D. Holde, *Chem.-Ztg.*, 1914, **38**, 241. H. Burstin and J. Winkler, *Przemysl Chem.*, 1928, **12**, 445; *Chem. Abs.*, 1928, **22**, 4786. *Erdöl u. Teer*, 1926, **5**, 26, 42, 62; *Chem. Abs.*, 1929, **23**, 2289. For a comparison of results on determination of asphalts in lubricating oils using benzines having slightly different physical properties, see E. A. Evans, *J. Inst. Pet. Tech.*, 1923, **9**, 384.

mixture of 80 parts of 96 per cent sulphuric acid and 20 parts of fuming acid (20 per cent SO_3). Garner[35] uses a benzine having d^{15} 0.680-0.690, aromatic hydrocarbon content of not more than 0.5 per cent and a distillation range (for at least 90 per cent) of 60-80°C. Other liquids which may serve as precipitants are acetone,[36] ethyl acetate[37] and methyl ethyl ketone saturated with water.[38] It is also reported that cyclohexane is not a satisfactory reagent since it dissolves a large proportion of the substances insoluble in benzine.[39] Nellensteyn and Roodenburg[40] propose ethyl ether as it is a homogeneous substance, does not require standardization and has a greater solvent power for hydroxy acids (due to oxidation) in asphalts than low-boiling hydrocarbons.

Removal of asphaltenes and other dark-colored substances from natural or artificial asphalts furnishes products which may be used in the manufacture of asphalt paper, lacquers, varnishes or paints.[41] The refining procedure consists in the addition of a liquid precipitant, such as pentane or aromatic-free gasoline. The asphalt solution may then be further treated with decolorizing agents, such as bleaching earths. Other agents which may be employed include sulphuric acid, anhydrous aluminum or ferric chloride, or boron fluoride.[41a] The latter materials are said to convert any dissolved asphaltenes into insoluble substances. In the case of mineral oils, warm dilute sulphuric acid (1 to 10 per cent)[42] may be used, or the liquid is allowed to stand in contact with aqueous solutions of heavy-metal salts, especially the chlorides.[43]

According to Rakovskii and Balashov,[44] 50 per cent sulphuric acid is the best strength for precipitation of asphaltenes from tar (from Pintsch retorts). In this instance the products are contaminated with phenols which may be separated by steam distillation.[45] In some instances, however, asphaltenes from acid sludges are reported to differ from normal asphaltenes in being soluble in basic solvents and being coagulated on heating to 100°C.[46] They are probably oxonium compounds derived from sulphuric acid. It is suggested that the composition for such derivatives may be represented by[47]



$$\begin{array}{c} HR'\text{—}O\text{—}R'' \\ \| \\ HSO_3H \end{array}$$

Hydrogenation of asphaltenes dissolved in hydrocarbon solvents converts them into resins or resin-like bodies.[48]

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[35] F. H. Garner, Private communication.

[36] F. Schwartz and H. Schluter, *Chem.-Ztg.*, 1911, **35**, 413.

[37] H. Kantorowicz, *Chem.-Ztg.*, 1913, **37**, 1438. The use of this liquid is contested by D. Holde and G. Meyerheim, *Chem.-Ztg.*, 1914, **38**, 241, 264.

[38] F. Schwartz, *Chem.-Ztg.*, 1911, **35**, 1417.

[39] M. Jakes, *Chem.-Ztg.*, 1923, **47**, 757; *Chem. Abs.*, 1924, **18**, 1047.

[40] F. J. Nellensteyn and N. M. Roodenburg, *Chem.-Ztg.*, 1930, **54**, 819; *Chem. Abs.*, 1931, **25**, 2278.

[41] J. W. le Nobel, U. S. P. 1,868,211, July 19, 1932, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1932, **26**, 5220. British P. 313,433 1928; *Brit. Chem. Abs.* **B**, 1930, 93. Dutch P. 24,396, 1931; *Chem. Abs.*, 1932, **26**, 1435.

[41a] *Cf.* use of pentane in deasphalting of mineral oils, discussed later in this chapter.

[42] R. N. Donaldson and R. McCollum, U. S. P. 1,506,115, Aug. 26, 1924, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1924, **18**, 3270.

[43] French P. 670,796, 1929, to N. V. Mijnbouw- en Cultuurmaatschappij "Boeten"; *Chem. Abs.*, 1930, **24**, 1970.

[44] V. E. Rakovskii and E. F. Balashov, *Khim. Tverdogo Topliva*, 1932, **3**, 180; *Chem. Abs.*, 1934, **28**, 5213.

[45] For the determination of asphaltenes in acid sludges by precipitation with benzene and benzene-alcohol mixture, see B. M. Ruibak and I. Bluymin, *Azer. Neft. Khoz.*, **1934**, No. 3, 27; *Chem. Abs.*, 1934, **28**, 7509.

[46] V. Kalichevsky and S. C. Fulton, *loc. cit.*

[47] S. Obryadchikov, *Neft. Khoz.*, 1928, **14**, 360; *Chem. Abs.*, 1928, **22**, 2264.

[48] S. C. Fulton and V. Kalichevsky, U. S. P. 2,006,199, June 25, 1935, to Standard-I. G. Co.; *Chem. Abs.*, 1935, **29**, 5543. French P. 744,220, 1933, to International Hydrogenation Patents Co., Ltd.; *Chem. Abs.*, 1933, **27**, 4109.

CARBENES

Such compounds have been described as those components of asphalt which are soluble in carbon disulphide (and certain other solvents, e.g., nitrobenzene or pyridine) but not in carbon tetrachloride.[49] The test for these substances (difference in solubility of the sample in carbon disulphide and tetrachloride) was devised to detect those asphalts which had been injured by weathering or by severe heat treatment during either refining or production, as carbene-formation appears to take place at temperatures of around 700° F.[50]

MacKenzie[51] observed that the quantity of carbenes (insoluble portion) increased when a solution of asphalt in carbon tetrachloride was allowed to stand and also when the solution was exposed to light. He suggested that "pure carbenes" be defined as those which are precipitated from carbon tetrachloride solution after 12 hours in the dark. "Pseudo carbenes" are those precipitated on exposure of the tetrachloride solution to light, generally for periods greater than 12 hours. He proposed the following theory: "That light acting upon a solution of bitumen in tetrachloride causes the bitumen to decompose, the tetrachloride giving hydrochloric acid, which in turn combines with unsaturated hydrocarbons and precipitates them." Both types of carbenes contained 3 to 4 per cent chlorine, and also nitrogen and sulphur. "Pure carbenes" did not melt at red-heat while the pseudo variety melted with effervescence at temperatures above 300°C. The effect of light, as mentioned by Mackenzie, was also noted by Alexander.[52]

The following procedure is suggested for determining carbenes in brown-coal generator tar:[53] 2 grams of the tar are dissolved in 30 cc. of benzene and to this solution (at 50°C.) are added 100-150 cc. benzine. The precipitate, after washing with benzine and drying, includes asphalts and insoluble material. The asphalts are separated by extraction with acetone, and to the latter solution is added excess carbon tetrachloride. This liquid mixture is then distilled until the temperature nearly reaches 77°C. (to remove acetone), after which the insoluble carbenes are filtered, washed, dried and weighed. A method for estimating asphaltenes, carbenes and carboids by etching the sample with benzine, carbon disulphide or tetrachloride and examining under the microscope is described by Schwartz.[54]

Carbenes are black solids, resembling coal in appearance and, like asphaltenes, they react with sulphuric acid to give sulphur-containing acidic derivatives.[55] The latter are soluble in pyridine and the solution may be diluted with water. Addition of mineral acids or salts of calcium, iron or silver to such diluted solutions precipitate the free acids or the corresponding salts, respectively. The sulphur derivatives are hydrolyzed by boiling with water or dilute alkalies with the liberation of sulphuric acid, but are stable towards alcoholic alkali.

CARBOIDS

These compounds are deep black in color like coal. In contrast to carbenes they are insoluble in carbon disulphide and probably represent a further stage in decomposition (polymerization or condensation) than carbenes.[56] Like the latter, carboids react with sulphuric acid to give acidic sulphur derivatives which are hydrolyzed by boiling with water or dilute hydrochloric acid. These sulphur compounds, however, are insoluble in pyridine and are decomposed by aqueous potassium hydroxide.

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[49] L. Kirschbaum, *Municipal Eng.*, 1909, **35**, 349; *Chem. Abs.*, 1909, **3**, 1212.
[50] C. Richardson and C. N. Forrest, *J. S. C. I.*, 1905, **24**, 310.
[51] K. G. MacKenzie, *Ind. Eng. Chem.*, 1910, **2**, 124.
[52] D. B. W. Alexander, *Ind. Eng. Chem.*, 1910, **2**, 242.
[53] B. G. Simek, *Mitt. Kohlenforschungsinst. Prag.*, **1932**, No. 3, 111; *Chem. Abs.*, 1932, **26**, 4445.
[54] F. Schwartz, *Allgem. österr. Chem. Tech.-Ztg.*, 1933, **51**, 41; *Chem. Abs.*, 1933, **27**, 4385.
[55] J. Marcusson, *Chem.-Ztg.*, 1918, **42**, 437; *J.S.C.I.*, 1919, **38**, 98A.
[56] J. Marcusson, *Chem.-Ztg.*, 1918, **42**, 437; *Chem. Abs.*, 1919, **13**, 2750; *Z. angew. chem.*, 1919, **32**, 113; *Chem. Abs.*, 1919, **13**, 2592.

Not only are carboids isolated from natural or petroleum asphalts, but they are also formed during certain hydrogenation operations.[57] For example, in the hydrogenation of shale tar (boiling 230-340°C.) the optimum temperature was found to be 440°C. since higher temperatures accelerated formation of carboids and coke.[58] Hydrogen pressure also exerts a considerable influence, lower pressures favoring the development of these bodies.[59]

ASPHALTOGENIC ACIDS

In addition to the four main constituents of asphalts previously mentioned, i.e., petroleum resins, asphaltenes, carbenes and carboids, another type of compounds present are the asphaltogenic acids or their anhydrides.[60] These are described as tar-like or resinous masses which are soluble in alcohol or chloroform, but nearly insoluble in petroleum ether. Their sodium salts are also sparingly soluble. The acids usually exhibit a specific gravity greater than 1, and contain variable proportions of sulphur. By continued heating at 200°C. they are transformed into the corresponding anhydrides and at higher temperatures substances resembling asphaltenes are formed. A comparison of the properties of some acids from Trinidad crude and from a Texas oil heated for 70 hours at 120°C., in air, is given in Table 219.

TABLE 219.—*Properties of Asphaltogenic Acids from Trinidad Crude Asphalt and from Heated Texas Oil.*

Acids from	Solubility in Petroleum Ether	Acid Value	Saponification Value	Iodine Value	Sulphur %
Trinidad crude asphalt .	Nearly insoluble	98.5	120 4	22.4	3 1
Texas oil.............	Nearly insoluble	89.3	147.0	17.3	1.2

The acids may be isolated in the following manner: The bitumen is dissolved in benzene (5 times the volume of asphalt) and the solution treated with neutral alcohol (8 times the volume of benzene). In this manner most of the neutral constituents are precipitated. The benzene-alcohol solution is decanted, neutralized with sodium hydroxide and then diluted with an equal volume of water. Unsaponifiable constituents are extracted with benzene, and the aqueous solution concentrated on a water bath. Asphaltogenic acids are liberated by acidifying with a mineral acid.

To secure the acid anhydrides, the unsaponifiable portion is united with the pitch-like substances precipitated by alcohol (in the first operation) from the benzene solution, and the mixture saponified with alcoholic potassium hydroxide in the presence of benzene. The resulting alcoholic solution of potassium soaps is diluted with water, extracted with benzene, concentrated, and then acidified with a mineral acid.

The formation of asphaltogenic, or polynaphthenic, acids by air oxidation of

[57] For the determination of carboid formed during hydrogenation, see I. Rapoport and M. Asipov, *Khim. Tverdogo Topliva*, 1933, **4**, 79; *Chem. Abs.*, 1934, **28**, 5626.

[58] I. Kluykvin, V. Efremov and F. Meshel, *Khim. Tverdogo Topliva*, 1932, **3**, 68; *Chem. Abs.*, 1934, **28**, 5645.

[59] I. S. Diner and M. S. Nemtzov, *Khim. Tverdogo Topliva*, 1932, **3**, 727; *Chem. Abs.*, 1934, **28**, 5645.

[60] J. Marcusson, *Z. angew. chem.*, 1916, **29**, 346, 349; *J.S.C.I.*, 1916, **35**, 1099; *Chem.-Ztg.*, 1914, **38**, 813, 822; *J.S.C.I.*, 1914, **33**, 739; *Mitt. Materialprüfungsamt*, 1918, **36**, 209; *Chem. Abs.*, 1921, **15**, 1806.

naphthene-containing petroleum distillates in the presence of alkali was observed by Charitschkov.[61] He described these acids as syrupy liquids, density 1.2, incapable of crystallizing, soluble in alcohol, chloroform, benzene, ether and carbon disulphide, and not being reduced by sodium amalgam. They gave a red coloration (like ketones) with sodium nitroprusside, reduced ammoniacal silver nitrate or Fehling's solution, and decomposed on distillation even under reduced pressure. As an example, oxidation of a kerosene fraction (boiling 169-171°C.), containing mainly one of the isomeric decanaphthenes, yielded an acid of the formula $C_{20}H_{25}O_4$.[62] The acid $C_{24}H_{34}O_4$ was obtained similarly from another decanaphthene fraction (boiling 164-168°C.). These products furnished viscous esters and on exposure to air (particularly in the presence of alkalies) resinified to asphalt-like bodies. Hence the name asphaltogenic acids. Charitschkov believed that at least two of the four oxygen atoms (in each acid molecule) were in hydroxy groups, and to the latter he attributed the pseudo acidic properties of the compounds. The presence of an aldehyde group (CHO) could not be proven.

Staeger[63] reports that asphaltogenic acids are obtained as some of the oxidation products of transformer oils. In agreement with Charitschkov, he considers them to be highly unsaturated, dihydroxy monocarboxylic acids. The exceptions appear to be the monohydroxy monocarboxylic acids resulting from the oxidation of mineral oils in the presence of lead as a catalyst. Rodman[64] and Brauen[65] observed the presence of polynaphthenic acids in transformer oils which had been subjected to long continual use. The latter investigator found the saponification number[66] of such bodies to be 187 and their molecular weights about 600.

It is interesting to note that a toxic effect of plant sprays (containing petroleum hydrocarbons) to foliage is ascribed by Tucker[67] to oil-soluble asphaltogenic acids. The latter are oxidation products resulting from the action of air and light on unsaturated hydrocarbons present in the spray. He believes that this toxic property can be attributed to the greater ease with which these acids pass through the walls of the leaf cell than the unoxidized oily portion and to their further breakdown into colloidal asphaltic bodies during which they absorb oxygen from the cells which they surround or into which they have gained entrance. Only a small proportion of acids (about 0.5 per cent) is required before injury to the foliage is apparent. Tucker suggests, therefore, that only oils having a low olefin content be employed in spray compositions and furthermore that such oils should be examined with respect to their resistance to oxidation in light.

ASPHALTS AS COLLOIDAL SYSTEMS

It is generally conceded that asphalts are colloidal systems but there are considerable differences of opinion as to the constitution of such systems. Sakhanov[68] suggested that asphalts are colloidal solutions of asphaltenes in tars and heavy oils and furthermore that carbenes and carboids are colloidal modifications of asphaltenes.[69] The latter being lyophilic with respect to aromatic hydrocarbons, terpenes, chlorinated hydrocarbons and carbon disulphide are dissolved by them forming highly dispersed and stable systems. On the other hand, as stated previously asphaltenes are lyophobic toward paraffin hydrocarbons and naphthenes and are coagulated by these substances.

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[61] K. W. Charitschkov, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1757; *J.C.S.*, 1909, **96** (1), 154. This procedure is suggested as a means of distinguishing aliphatic and naphthenic hydrocarbons, the former being only slightly oxidized and the latter yielding polynaphthenic acids.

[62] K. W. Charitschkov, *Chem.-Ztg.*, 1909, **33**, 1165; *J.C.S.*, 1909, **96** (1), 896; *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 345; *J.C.S.*, 1909, **96** (1), 471.

[63] H. C. Staeger, *Ind. Eng. Chem.*, 1925, **17**, 1272.

[64] C. J. Rodman, *Elec. World*, 1922, **79**, 1271.

[65] W. Brauen, *Elektrotech. Z.*, 1914, **35**, 145.

[66] A method for determining saponification numbers of petroleum asphalts is outlined by J. H. Bruun and L. W. Claffey, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 255; *J. Inst. Pet. Tech.*, 1936, **22**, 498A; *Chem. Abs.*, 1936, **30**, 6180.

[67] R. P. Tucker, *Ind. Eng. Chem.*, 1936, **28**, 458.

[68] A. N. Sakhanov, *Neft. Slantsevoe Khoz.*, 1924, **7**, 933; *Chem. Abs.*, 1925, **19**, 3158.

[69] A. N. Sakhanov, *Petroleum Z.*, 1925, **31**, 1441; *J.S.C.I.*, 1925, **44**, 745B.

Nellensteyn[70] advances the theory that asphalts contain elemental carbon in colloidal form, the latter being the essential constituent. In other words, the asphaltene micella may be viewed as a carbon nucleus enveloped in hydrocarbons. Evidence for this was based on the synthesis of asphalt-like bodies (carbon organosols) by the electrical dispersion of carbon in carbon tetrachloride, in this liquid containing 5 per cent of an asphalt-base oil or protective bodies extracted from asphalt, or in liquid paraffin or an asphalt-base oil distillate. Brown, stable sols were obtained whenever protective bodies were present, otherwise gray-black, unstable colloidal solutions resulted. However, the latter could be stabilized and the color changed to brown by incorporation of protective agents. Furthermore, the dispersed phase (after filtering off large particles which were always formed) could be separated by addition of benzine (boiling 40-60°C.).

Further substantiation of this theory was secured by ultramicroscopical examination of natural asphalt (from Trinidad) and Persian, Mexican and Borneo petroleum asphalts.[71] Of the three latter, the first was an oxidized asphalt and the other two were prepared by distillation of corresponding asphalt-base crude oils. All of the materials exhibited the Brownian movement, this being very slow when a viscous medium (lubricating oil) was employed, but intense when benzene, toluene or carbon disulphide was the diluent. As viewed under the ultramicroscope lyophobic ultramicrons appear to be strongly protected and assume the properties of lyophilic sols with regard to reversibility in solubility and decrease of sensitivity to flocculating agents. It was believed that in asphalt solutions there are present highly protected lyophobe sols, showing reversibility because of protectors, and the ultramiscroscopic image is due to lyophobe carbon particles.

If asphalt be considered as consisting of three principal groups of components:

1. the medium
2. a lyophile part: the protective bodies
3. a lyophobe part: the elemental carbon

and the dispersed phase (or asphalt micelles) consisting of the last two groups, then the stability of the system depends upon the relation between the micelles and oily medium. According to Nellensteyn[72] the most important factor affecting stability is the interfacial tension. When this is decreased (e.g., by the addition of benzine) flocculation or precipitation occurs due to the joining of particles of the dispersed phase. Liquids of low surface tension (17 to 24 dynes per cm.), such as benzine, ether, *n*-hexane or acetone, are flocculating agents. Those possessing higher surface tensions (27 to 36 dynes per cm.), such as benzol, carbon disulphide and pyridine, are peptizing agents. Nellensteyn points out that in the standardization of normal benzine as a precipitant (for the analysis of asphalts) its surface tension should be considered as well as its boiling range and gravity. He also believes that the action of carbon tetrachloride on carbenes (i.e., precipitation) may be explained by the fact that the surface tension of this chloride (25.7 dynes per cm.) places it in a class intermediate between precipitating and peptizing agents. For this reason the tetrachloride affects only the less stable micelles. The latter would be formed by decomposition as for example by overheating, distillation or air-blowing.

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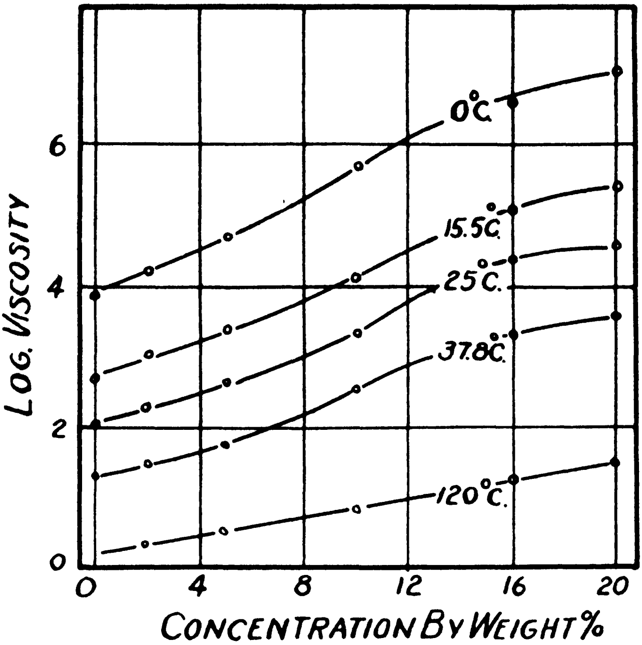
[70] F. J. Nellensteyn, *J. Inst. Pet. Tech.*, 1924, 10, 311.

[71] F. J. Nellensteyn and A. J. P. van der Burgh, *J. Inst. Pet. Tech.*, 1925, 11, 346.

[72] F. J. Nellensteyn, *J. Inst. Pet. Tech.*, 1928, 14. 134. *Asphalt u. Teer*, 1935, 35, 200, 233, 281, 303; *J. Inst. Pet. Tech.*, 1935, 21, 205A.

Pfeiffer and van Doormaal[73] agree with other investigators that asphalts may be considered as colloidal systems, and suggest that the latter consist of asphaltenes dispersed in maltenes.[74] These two constituents may be readily separated by treatment of asphalt with benzine (boiling 60 to 80°C.). The dispersed phase or asphaltenes (benzine-insoluble) are believed to consist of high-molecular hydrocarbons which are predominantly aromatic or hydroaromatic in character, having a comparatively low hydrogen content, and formed by polymerization and dehydrogenation of lower-molecular hydrocarbons. The dispersing medium or maltenes (benzine-soluble portion) governs the rheological properties of asphalts.



Courtesy Journal of Physical Chemistry

FIG. 299.—Concentration Plotted Against Logarithm of Viscosity for Solutions of Asphaltenes in Petrolenes. Viscosity at 120°C. in poises; others in g.sec.cm.$^{-2}$ (C. Mack)

When the maltenes are highly aromatic (or hydroaromatic) the asphaltenes are so well peptized that the resulting compositions flow readily and can be classed as purely viscous materials. Maltenes of slightly lower peptizing power give rise to products which exhibit a somewhat plastic character and which may be designated as normal types. If the peptizing action of the dispersing medium be further reduced, due either to low aromatic content of the crude oil serving as the source material or to the elimination of aromatics and hydroaromatics by air-blowing, then the resulting asphalt has a strongly plastic character.

These conclusions were substantiated (at least in part) by extracting maltenes from asphalts representing the three classes mentioned above. Asphaltenes of the same type were then dissolved in each of three maltenes. In each instance the rheological property of the asphalt so-made corresponded to that shown by the sample from which the maltenes were obtained initially.

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[73] J. P. Pfeiffer and P. M. van Doormaal, *J. Inst. Pet. Tech.*, 1936, **22**, 414; *Chem. Abs.*, 1936, **30**, 6545; *Brit. Chem. Abs.* **B**, 1936, 774; *J. Inst. Pet. Tech.*, 1936, **22**, 362A.

[74] Maltenes are also known as petrolenes.

According to Mack,[75] petroleum asphalts may be considered as a dispersion (lyophilic sol) of asphaltenes in petrolenes (asphaltic resins and oily constituents), though carbenes, carboids and asphaltic acids (or their anhydrides) may be present also in small proportions. Viscosity measurements, particularly relative viscosities, indicated, however, that at high temperatures (120°C.) liquid asphalts behaved as ideal solutions. Such measurements were made on solutions (in the same petrolenes) of asphaltenes derived from asphalt by precipitation with petroleum ether.[76] The falling cylinder method was employed.[77] The apparatus consisted of two vertical coaxial cylinders. Asphalt was placed between the cylinders, weights placed on the outer cylinder and the velocity with which it moved was measured. Viscosity was calculated according to the formula

$$N = \frac{P}{2\,LV}\ln\frac{R_2}{R_1}$$

in which N = the viscosity in poises, P = total weight, V = velocity, L = height of asphalt, and R_2 and R_1 = radii of the outer and inner cylinders, respectively.[78]

The viscosity of solutions of asphalts, varying in concentration from 2 to 20 per cent, are shown graphically in Fig. 299. Relative viscosities, i.e., the viscosity of the solution divided by that of the solvent, are given in Table 220.

TABLE 220.—*Relative Viscosities of Solutions of Asphaltenes in Petrolenes.*

% Concentration	Relative Viscosities at 0°C.	15.5°C.	25°C.	37.8°C.	120°C.
2	2.137	2.136	1.82	1.552	1.353
5	6.76	5.281	4.23	3.00	2.09
10	71.82	28.81	20.01	19.37	4.312
16	596.4	294.1	201.8	116.2	11.45
20	1792.3	592.9	367.0	224.2	20.12

Mack has also shown that the molecular weight of the solute (asphaltenes) may be calculated from the relative viscosity by application of the formula

$$\log \textit{relative viscosity} = kcM$$

in which k is a constant, c is concentration in per cent by weight, and M is the molecular weight. By the use of this equation and the above data, the molecular weight of the asphaltenes investigated was shown to be 1800 at 120°C. (See Table 221.) At lower temperatures the values ranged from about 3000 to 5000.[79] Mack believes these latter values can be attributed to association of the asphaltene molecules. Furthermore, this phenomenon (association) is responsible for the high relative viscosities (at low temperatures) rather than solvation.

PREPARATION OF ASPHALT FROM PETROLEUM

As previously mentioned, the high-boiling residues from distillation or cracking operations are the source of petroleum asphalts. The quality of the product so

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[75] C. Mack, *J. Phys. Chem.*, 1932, **36**, 2901.

[76] In this connection C. Mack (*loc. cit.*) points out that after precipitation and filtration the asphaltenes must be kept dissolved in benzol, otherwise on drying they become insoluble in solvents.

[77] This was devised by A. Pochettino, *Nuovo cimento*, 1914, **8**, 77.

[78] The term *ln* serves to indicate natural logarithm or $\log_e$.

[79] Values of 5000-6000 had been reported previously for asphaltenes from Russian crude oils; A. Sachanov, *Neft. Khoz.*, 1924, **7**, 933; *Chem. Zentr.*, 1925, **1**, 1828.

TABLE 221.—*Molecular Weight and Degree of Association of Asphaltenes in Petrolenes.*

	At 0°C.			At 25°C.			At 120°C.	
% Conc. of Solution	Value of *kM*	Molecular Weight	Degree of Association	Value of *kM*	Molecular Weight	Degree of Association	Value of *kM*	Molecular Weight
2	0.16496	4580	2½	0.1301	3610	2	0.06568	1820
6	0 1650	4580	2½	0.12531	3480	2	0.0640	1780
10	0.1856	5160	3	0.13012	3610	2	0.0635	1760
16	0.17347	4820	2⅜	0.14405	4000	2¼	0.0662	1830
20	0.16267	4520	2½	0.12823	3560	2	0.0652	1810

prepared is affected by the distillation operation and by the presence of free carbon.[80] When the latter is in a colloidal state it exerts no deleterious action, but if merely suspended (e.g., due to overheating during distillation) in the asphalt then an inferior product is the result. It is reported that the material made from asphaltic-base crudes in a shell still has a higher softening point than that made in a pipe still[81] for a given penetration of the asphalt. This may be accounted for by the low resin and asphaltene contents and high proportions of hard asphalt and coke. Paraffin base oils on straight distillation yield a residue consisting of oil, asphalt, coke and solid paraffins, the latter being disadvantageous if the percentage of resins and asphaltenes is low.[82] Such oils, however, furnish satisfactory asphalts if they are first subjected to mild cracking, that is not severe enough to form coke.

Ichikawa[83] reports that in the steam-refining of petroleum asphaltic residua much better products, especially with respect to cementing and tensile strengths, are obtained if a large rather than a small volume of steam is employed. Distillation at low pressure (2 mm.), however, was considered as the best method of manufacture.

Egloff and Morrell[84] point out that cracking can be controlled so as to permit production (10 to 20 per cent) of asphalt in addition to high yields of gasoline from paraffin-base charging stocks (e.g., Pennsylvania crude oils) which have low sulphur contents. Because of the absence of this latter element, and also oxygen, they believe that under these conditions asphalt formation is the result of condensation and polymerization accompanied by dehydrogenation. By subsequent blowing operations (with air or steam) the cracked asphaltic residues can be made to meet many specifications.

Another procedure for making asphalt includes dissolving the oil, or distillation residues, in liquid aliphatic esters or ethers, and then cooling the mixture so that both the paraffin wax and hard asphalt are precipitated.[85] Ethyl acetate, methyl butyrate or propionate or diisopropyl ether are appropriate liquids. After separation of the insoluble portion by filtration the liquid can be subjected to distillation to secure the soft asphalt.

The effects of continuous heating, for 70 days at 170°C., on the properties of two asphalts (m.p. 32.8°C. and 41.1°C.) from Mid-Continent crudes were investigated by Sikes and Corey.[86] They found that the acid value, after an initial increase, decreased considerably, which may be attributed to loss of volatile acids. Ductility and penetration also decreased rapidly while an increase was noted in the softening point and viscosity. The flash point was not altered much, and the solubility of the asphalt in carbon disulphide remained between 99.6 and 99.9 per cent.

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[80] R. Fussteig, *Asphalt u. Teer,* 1935, **35**, 627; *J. Inst. Pet. Tech.*, 1935, **21**, 377A.

[81] The advantages of pipe still operation (distillation under reduced pressures with lower temperatures and heating periods) over batch operation are discussed by N. Mayer, *Chem.-Ztg.*, 1935, **59**, 456; *J. Inst. Pet. Tech.*, 1935, **21**, 308A; *Brit. Chem. Abs.* **B**, 1935, 757.

[82] Determination of paraffin in asphalts is discussed by V. Parini, *Neft.*, 1933, **4** (5), 18; *Chem. Abs.*, 1935, **29**, 2726; *Brit. Chem. Abs.* **B**, 1935, 1028.

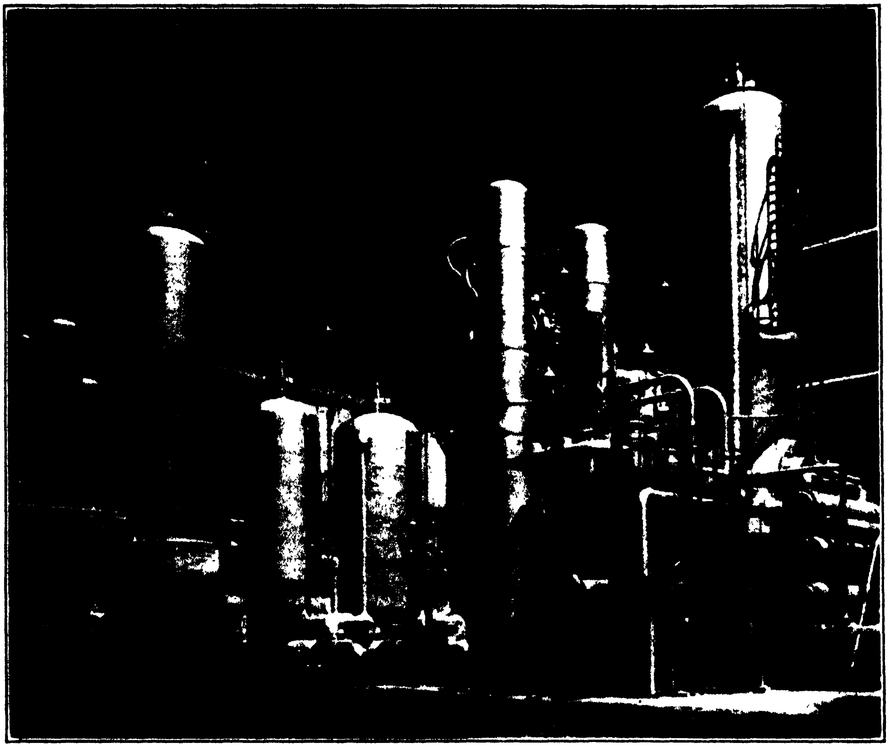
[83] Y. Ichikawa, *J. Soc. Chem. Ind. Japan*, 1936, **39**, Suppl. bind., 129, 161; *Chem. Abs.*, 1936, **30**, 5402; *Brit. Chem. Abs.* **B**, 1936, 626, 676.

[84] G. Egloff and J. C. Morrell, *Ind. Eng. Chem.*, 1931, **23**, 679. See also, J. C. Morrell, U. S. P. 2,004,210, June 11, 1935, to Universal Oil Products Co.; *J. Inst. Pet. Tech.*, 1935, **21**, 313A.

[85] K. Kell and W. H. Schmitz, French P. 783,443, 1935; *Chem. Abs.*, 1935, **29**, 8318. British P. 443,287, 1934; *Brit. Chem. Abs.* **B**, 1936, 485.

[86] A. W. Sikes and C. H. Corey, *Ind. Eng. Chem.*, 1935, **27**, 192; *Brit. Chem. Abs.* **B**, 1935, 885; *Chem. Abs.*, 1935, **29**, 2725.

Low-boiling petroleum hydrocarbons, e.g., benzine, have been proposed as solvents for the extraction of heavy oils from petroleum asphalts.[87] According to Stratford and Pokorny,[88] such light hydrocarbons may be admixed with methyl, ethyl, propyl, isopropyl or cyclic alcohols. Zwergal[89] treated asphalts with methyl, ethyl, propyl, butyl and amyl alcohols successively. He observed that the extracts obtained with the first two alcohols were oily and resinous, while those with the last two were coke-like. Those constituents which were soluble in propyl alcohol possessed the highest carbon and hydrogen and lowest sulphur and oxygen contents, and exhibited the highest ductility.



Courtesy Union Oil Co. of California

FIG. 300.—Plant for Deasphalting and Dewaxing with Liquid Propane. Tall column at left is for deasphalting; unit at right is for dewaxing.

Treatment of asphaltic oils with a normally gaseous hydrocarbon,[90] e.g., propane,[91] at temperatures and pressures at which the latter is liquid, results in the precipitation of asphalt.[92] This product is said to have a lower carbene content and higher solubility in naphtha (86°Bé.) than that obtained by distillation of the oil. When both wax and asphalt are present in the petroleum fraction, after precipitation of asphalt the pressure is released and some propane evaporated, thus chilling the oil and effecting separation of wax.[93] Following removal of the oil, the mixed precipitate is treated with liquid propane at a temperature sufficiently high to dissolve the wax. By adjusting conditions and methods of treatment of this type of oil, asphalt and wax can be precipitated separately or simultaneously.[94] Also, separation of soft and hard asphalts may be made in this manner.[95] Fractions of petroleum oils, resins and asphaltenes, obtained by treatment of petroleum residues with propane, may be remixed in proper proportions to give asphalts of the desired physical properties.[96]

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[87] British P. 437,843, 1935, to N. V. Machinerieen-en Apparaten Fabriken "Meaf"; *Chem. Abs.*, 1936, 30, *2747*.

[88] R. K. Stratford and O. S. Pokorny, Canadian P. 353,486, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1935, 29, 8322.

[89] A. Zwergal, *Oel, Kohle, Erdöl, Teer*, 1935, 11, 608; *Chem. Abs.*, 1935, 29, 8309; *J. Inst. Pet. Tech.*, 1935, 21, 401A.

[90] For use of natural gas under pressure to fractionate crude oil or heavy residues into asphalts, resins and oils, see S. v. Pilat, *Przemysl Naftowy*, 1935, 10, 661; *Chem. Abs.*, 1936, 30, 6542.

Instead of using liquefied propane alone, the solvent may consist of this hydrocarbon and approximately 40 per cent of ethane.[96a] Partial precipitation of asphalt and complete elimination of wax are secured by dilution of distillates (from hydrogenation operations) with 20 per cent by weight of liquid butane.[97] von Pilat[98] reports that a liquid, propane-butane mixture (61.2 per cent propane, 34.36 per cent isobutane and 4.17 per cent *n*-butane) removed only part of the asphalt from petroleum residues. By introducing dry natural gas, containing about 97 per cent methane, into the liquid mixture (until the pressure had risen to 30 atmospheres) almost complete separation of asphalt took place. Continued introduction of methane, until the pressure increased to 130 atmospheres, effected a step-wise fractionation of the oily portion, the higher-molecular weight hydrocarbons separating first and then those of lower molecular weights as the proportion of methane was increased.[99]

Ellis[99a] suggests treatment of hydrocarbon oils by mixing a stream of such oils with a stream of liquefied hydrocarbon gases (e.g., 75 per cent propane and 25 per cent ethane) at 20 atmospheres pressure and 75°F. to cause precipitation of asphaltic bodies, subsequently cooling the treated oil solution to about 20° to — 10°F. to remove wax and then releasing the pressure to rid the oil of the liquefied gas.

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[91] For discussions of the use of liquid propane in dewaxing, deasphalting and other refining operations, see R. E. Wilson, P. C. Keith, Jr., and R. E. Haylett, *Ind. Eng. Chem.*, 1936, **28**, 1065; *Trans. Am. Inst. Chem. Eng.*, 1936, **32**, 365; *Chem. Abs.*, 1936, **30**, 8585; *J. Inst. Pet. Tech.*, 1936, **22**, 455A; *Brit. Chem. Abs.* **B**, 1936, 775. A. P. Anderson, H. O. Forrest and L. Van Horn, *Refiner*, 1936, **15**, 210; *Nat Pet. News*, 1936, **28** (21), 49; *Oil and Gas J.*, 1936, **35**, 103; *Chem. Abs.*, 1936, **30**, 5773, 6176; *J. Inst. Pet. Tech.*, 1936, **22**, 358A.

[92] U. B. Bray, U. S. P. 1,988,714, Jan 22, 1935, to Union Oil Co. of Calif.; *Chem. Abs.*, 1935, **29**, 1624. See also, U. S. P. 2,010,007 and 2,010,008, Aug. 6, 1935; *Chem. Abs.*, 1935, **29**, 6420; *J. Inst. Pet. Tech.*, 1935, **21**, 383A. U. B. Bray and C. E. Swift, U. S. P. 2,006,092 to 2,006,097, June 25, 1935, to Union Oil Co. of Calif.; *Chem. Abs*, 1935, **29**, 5648; *Brit. Chem. Abs.* **B**, 1936, 731, 1139. U. B. Bray, U. S. P. 2,006,098, June 25, 1935; *Chem. Abs.*, 1935, **29**, 5649; *Brit. Chem. Abs.* **B**, 1936, 731. M. Pier and A. Eisenhut, U. S. P. 2,055,135, Sept. 22, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 7837. W. H. Bahlke, F. W. Sullivan, Jr., and R. E. Wilson, U. S. P. 2,086,487, July 6, 1937, to Standard Oil Co. of Ind.

[93] U. B. Bray, Canadian P. 352,059, 1935, to Union Oil Co. of Calif.; *Chem. Abs.*, 1935, **29**, 7068. U. S. P. 2,049,046, July 28, 1936; *Chem. Abs.*, 1936, **30**, 6550.

[94] U. B. Bray, U. S. P. 2,041,275; 2,041,277, May 19, 1936, to Union Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 4664.

[95] B. G. Aldridge and B. Hopper, U. S. P. 2,041,278, May 19, 1936, to Union Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 4664.

[96] French P. 800,144, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 8602.

[96a] U. B. Bray and C. E. Swift, U. S. P. 2,040,239, May 12, 1936, to Union Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 4664; *J. Inst. Pet. Tech.*, 1936, **22**, 319A.

[97] British P. 445,898, 1934, to International Hydrogenation Patents Co., Ltd.; *Brit. Chem. Abs.* **B**, 1936, 679.

[98] S. von Pilat, *Oil and Gas J.*, 1936, **35** (10), 54. See also M. Naphtali, *Refiner*, 1936, **15**, 116; *J. Inst. Pet. Tech.*, 1936, **22**, 314A.

[99] For a discussion of the fractionation of oils in this manner, see Chapter 1.

[99a] Carleton Ellis, U. S. P. 2,081,174, May 25, 1937, to Standard Oil Development Co.

Other extractants proposed include phenol, furfural,[100] cyclic nitrogen compounds, e.g., pyrroles, indoles, quinolines or piperidines,[101] and mixtures of secondary or tertiary aliphatic alcohols, e.g., *ter*-butyl, with water, alcohols or ketones.[102] Such aliphatic ethers as ethyl, isopropyl, butyl or amyl and esters of the corresponding alcohols with the lower fatty acids (formic to capric) are said to act as selective solvents for soft asphalt constituents, causing precipitation of the hard asphalt resin and also paraffin wax.[103] For obtaining high-grade asphalt from Mid-Continent crude oils it is suggested that residua from such crudes, containing constituents heavier than gas oil, be subjected to selective solvent action of furfural, nitrobenzene or sulphur dioxide, the insoluble portion furnishing lubricating oil stock and the soluble fraction a source of asphalt.[104]

OXIDIZED ASPHALTS

Oxidation, or air blowing, is often found to be the most desirable method of finishing many of the asphalts obtained from petroleum.[105] The exact nature of the reactions taking place during such operations is not definitely known and there is need of considerable investigation in this direction. Lahocinski[106] oxidized asphalts (from Polish crude oils) which he considered to consist of resins, asphaltenes and oil plus paraffin wax. Although the materials contained different proportions of the three ingredients, nevertheless the effect in each instance was the same, viz., diminution of the oil and resin contents and an increase of the asphaltene fraction. The latter influenced the melting point of the asphalt. He believed that the resin fraction was the carrier of all fundamental properties of asphalt, while the oil fraction exhibited no such characteristic properties.

Thurston and Knowles[107] have investigated the oxygen absorption of various constituents of asphalt (238 penetration at 25°C.) from Mexican petroleum. The following method of separation was employed. *Asphaltous acids and anhydrides* were extracted by dissolving the specimen in benzene and refluxing with aqueous alcoholic potash. Afterwards the alcohol layer was separated, acidified and the acids dissolved in ether. Evaporation of the latter yielded a brown, sticky mass. *Asphaltenes* were obtained by precipitation with straight-run Pennsylvania naphtha (88°Bé.) using 40 volumes to 1 of asphalt. Extraction of the precipitate with more naphtha eliminated occluded resins. Asphaltenes do not melt but swell and decompose on heating. According to Thurston and Knowles, asphaltenes are the essential constituents of asphalt, distinguishing it from other petroleum products, and are responsible for its plastic properties.

After separation of acids and asphaltenes, the remaining "petrolenes" were treated with fuller's earth, and the latter then extracted successively with naphtha, carbon disulphide and benzene to secure *oils, petroleum resins* and *asphaltic resins,* respectively. Both of these resins have moderate drying properties when exposed to air in thin films, and this is more pronounced with asphaltic resins which are the heavier and more viscous. No *carbenes* or *carboids* were present in the specimen tested. The analytic data are summarized in Table 222.

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[100] A. A. Wells, U. S. P. 2,010,423, Aug. 6, 1935, to Standard Oil Development Co.; *Chem. Abs.*, 1935, **29**, 6420; *Brit. Chem Abs.* **B**, 1936, 583; *J. Inst. Pet. Tech.*, 1935, **21**, 383A. French P. 753,036, 1933; *Chem. Abs.*, 1934, **28**, 892.

[101] French P. 800,473, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 8597.

[102] British P. 450,511, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1937, **31**, 249; *Brit. Chem. Abs.* **B**, 1936, 969; *J. Inst. Pet. Tech.*, 1936, **22**, 455A.

[103] K. Kell and W. H. Schmitz, British P. 443,287, 1936, *Chem. Abs.*, 1936, **30**, 5407; *Brit. Chem. Abs.* **B**, 1936, 485.

[104] R. R. Thurston, Canadian P. 359,103, 1936, to Texaco Development Corp.; *Chem. Abs.*, 1936, **30**, 6181.

[105] P. Hubbard, *J.S.C.I.*, 1929, **48**, 108T. For descriptions of a number of methods for oxidizing petroleum oils or residues to asphalts, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. For description of a plant for manufacturing asphalts from Mid-Continent oils, see H. B. Batchelor, *Oil and Gas J.*, 1934, **33** (15), 18; *J. Inst. Pet. Tech.*, 1934, **20**, 615A.

[106] Z. Lahocinski, *Przemysl Naftowy*, 1933, **8**, 229; *Chem. Abs.*, 1933, **27**, 4065.

[107] R. R. Thurston and E. C. Knowles, *Ind. Eng. Chem.*, 1936, **28**, 88; *J. Inst. Pet. Tech.*, 1936, **22**, 106A; *Brit. Chem. Abs.* **B**, 1936, 306; *Chem. Abs.*, 1936, **30**, 2739.

TABLE 222.—*Constituents of Soft Mexican Asphalt.*

	Original Asphalt	Acids	Asphaltenes	Asphaltic Resins	Petroleum Resins	Oils
Yield, %	100	0.3	28.0	15.7	22.0	34.0
Sp. gr. (25°C.)	1.024	—	1.167	0.995	0.995	0.946
Iodine value	51	—	65	52	55	42
Sulphur, %	6.1	—	8.09	8.55	5.6	4.04
Carbon	85.05	—	79.61	82.19	82.70	85.39
Hydrogen	10.38	—	7.79	10.38	10.89	11.39
Ash	0.27	—	0.59	Trace	0.0	0.0
Sol. in CS_2	99.7	—	—	—	—	—
Sol. in CCl_4	99.7	—	—	—	—	—

The rates of absorption of oxygen by the asphalt and also its constituents were measured (using 1 g. samples mixed with sand, at 200°C. for 3 hours) and these increased progressively with oily constituents, petroleum resins, asphaltic resins and asphaltenes. Also the quantity of oxygen absorbed was determined, and that recovered as water or carbon dioxide. Asphaltenes proved to be the most readily oxidized and oils the most resistant. Data obtained in the latter instance are given in Table 223. Some oxygen was used in the formation of alcohols, aldehydes and ketones, which were not measured but included under the heading "unaccounted for." Asphaltenes from oxidized asphalts did not react with oxygen any more readily than those from soft asphalts. Those obtained from air-blown cracked residuum, however, were the least reactive of any investigated.

TABLE 223.—*Oxidation of Constituents from Soft Mexican Asphalt.*

	Original Asphalt	Asphaltenes	Asphaltic Resins	Petroleum Resins	Oils
Oxidation:					
Oxygen used, % of sample	17.3	23.6	1.85	15.4	13.4
Change in weight, % of sample	−5.0	+2.7	−2.3	−3.67	−2.8
Oxygen used:					
Absorbed by sample, %	—	23.6	—	—	—
Recovered as H_2O	67.9	59.6	71.3	72.1	71.5
Recovered as CO_2	14.2	12.9	10.7	9.2	8.9
Unaccounted for	17.9	3.9	18.0	18.7	19.6

Thurston and Knowles suggest that oxidation may take place in three ways:

1. Addition of oxygen, which forms unstable compounds from which water is eliminated, leaving unsaturated compounds which polymerize.

2. Oxidation with the formation of carboxyl derivatives from which carbon dioxide is eliminated, followed by polymerization.

3. Elimination of volatile oxidation products other than water and carbon dioxide from the above types of unstable oxygen compounds, followed by polymerization.

These investigators also report that oxidation of asphaltenes results in the formation of carboids, 96 per cent conversion being obtained at 200°C. (for 3 hours) and 68 per cent at 150°C. In the absence of oxygen, at 150°C., 7 per cent transformation was effected. This indicated that oxidation and not merely heat polymerization was the essential reaction. Typical analyses of asphaltenes (from hard steam-reduced Mexican asphalt) and of the carboids from them by oxidation are given in Table 224.

TABLE 224.—*Asphaltenes and Carboids from Steam-reduced Mexican Asphalt.*

	Asphaltenes	Carboids
Carbon	81.50	74.25
Hydrogen	7.50	5.13
Sulphur	8.60	8.16
Chlorine	Trace	—
Ash	0.51	0.50
Nitrogen	1.16	1.10
Oxygen	0.73	10.86
Sol. in CS_2, %	99.7	3.0
C:H ratio	10.9	14.5
Saponification value	6.4	124
Acid value	3.0	4.0

That asphalts made by air oxidation do not contain carboids was explained on the basis that the usual conditions of oxidation are not as severe as those in the above tests. Furthermore, during treatment the asphaltenes are not isolated and exposed intimately to the action of oxygen but remain dissolved in oils and resins.

A number of methods, differing essentially in construction details, have been suggested for the preparation of oxidized asphalts. Manheimer[108] points out that oxidation in tanks requires long periods of time, only a moderate period in batch stills, a short time in continuous shell stills, and is effected quickest in towers. The fundamental factors are (1) temperature, (2) air-blast, (3) nature of the initial product, (4) the oxidation surface, (5) carbon separation and (6) height of the liquid column. The temperature required varies with the composition of the charging stock, an average of 235-260°C. for paraffin base, 230-245°C. for asphalt base, while 220°C. is sufficient if the charge has a large proportion of soft asphalt. In addition to asphalt, gas and gas oil are the main by-products.

Gard and Aldridge[109] suggest heating the oil in a still and circulating hot oil through a heat-exchanger and back into the still. Before entering the heat-exchanger air is introduced into the hot body of oil and at the same time steam is forced into the liquid through a perforated pipe in the bottom of the still. By controlling the rate of air and steam supply and the temperature by the heat-exchanger, asphalt of a desired melting point, penetration and ductility may be obtained. In another operation, the hot residuum from a pipe still is mixed with air, and then conducted into a reaction chamber.[110] The temperature in the latter is regulated by cooling coils through which a portion of feed stock is passed. The same effect is accomplished by adding a liquid heat-absorbing medium, such as water or oil, which has a boiling point lower than the reaction temperature.[111] Before subjection to oxidation the residuum may be blended with cylinder oil having a viscosity (at 99°C.) of 190 seconds Saybolt.[112]

After being heated to high temperatures (about 220°C.), the asphaltic petroleum residue is conducted through a series of compartments in each of which air is supplied below the surface of the liquid.[113] Any vapors formed are removed and passed through a condenser. Catalysts which may be employed include spent clarifying and decolorizing agents (e.g., clays) from petroleum oil refining[114] and sulphuric acid mixed with persulphates or perborates.[115] In the latter instance reaction may be effected at 130°C. More intimate contact between the reactants is secured by forcing air through a porous ceramic diaphragm (before mixing with the heated hydrocarbon) thus transforming it into a state of minute subdivision[116] or by passing atomized petroleum residuum countercurrent to a hot air stream.[117]

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[108] J. Manheimer, *Petroleum Z.*, 1935, **31** (40), 4; *Chem. Abs.*, 1936, **30**, 2740.

[109] E. W. Gard and B. G. Aldridge, U. S. P. 1,999,018, Apr. 23, 1935; *Brit. Chem. Abs.* **B**, 1936, 357; *J. Inst. Pet. Tech.*, 1935, **21**, 223A. See also U. S. P. 1,953,345 and 1,953,346, Apr. 3, 1934; *Chem. Abs.*, 1934, **28**, 3890. R. T. Howes and C. N. Whitaker, *Refiner*, 1935, **14**, 102; *J. Inst. Pet. Tech.*, 1935, **21**, 171A.

[110] C. P. McNeil, U. S. P. 1,942,656, Jan. 1, 1934, to Standard Oil Co. of Indiana; *Brit. Chem. Abs.* **B**, 1934, 951. *Cf.* C. P. McNeil and S. A. Montgomery, U. S. P. 2,032,546, Mar. 3, 1936, to Standard Oil Co. of Indiana; *Chem. Abs.*, 1936, **30**, 2747.

[111] B. G. Aldridge, U. S. P. 1,988,766, Jan. 22, 1935, to Union Oil Co. of Calif.; *Chem. Abs.*, 1935, **29**, 1624.

[112] B. L. Rose, U. S. P. 2,028,922, Jan. 28, 1936, to Standard Oil Co. of Ohio; *Chem. Abs.*, 1936, **30**, 1994.

Stratford[118] proposes as raw material, for the manufacture of oxidized asphalts, the extracts obtained by treating petroleum oils with selective solvents, e.g., phenol, aniline, sulphur dioxide or furfural. Hydrocarbons procured in this manner may be subjected to air-blowing at 200°C. and under a pressure of 50 lbs. per sq. in.[119]

After oxidation at relatively low temperatures (175°C.) the asphaltic product is subsequently maintained at a higher temperature (350°C.) to effect polymerization of oil fractions.[120] The latter operation may be conducted under pressure sufficient to prevent distillation of vaporizable oil fractions. When cracked residuum, relatively high in unstable compounds insoluble in carbon tetrachloride, is heated and air-blown it may then be blended with uncracked residue which has been similarly treated.[121] In this manner unstable constituents are reported to be stabilized and their segregation inhibited.

Bray and Beckwith[122] treat oxidized asphalt with benzine or liquid propane to extract oily components. Afterwards the bitumen fraction may be mixed with an oil possessing different characteristics than that separated. Or the separated oil may be subjected to the action of liquid sulphur dioxide.[123] The extract thereby obtained is blended with the asphalt and the mixture is air-blown. In this way a product of high susceptibility to temperature changes is made.

The use of air containing a small proportion of chlorine is recommended by Douthett.[124] Asphalts are secured which have a high melting point for a given consistency and contain only about 0.5 per cent chlorine, but are free of undesirable non-volatile decomposition products.[125] Hoover[126] proposes adding a small pro-

[113] S. Tijmstra, U. S. P. 1,975,563, Oct. 2, 1934, to Shell Development Co.; *Chem. Abs.*, 1934, **28**, 7520. French P. 791,278, 1935, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 3226.

[114] W. A. Craig and F. E. Griffith, U. S. P. 1,997,569, Apr. 16, 1935, to W. C. McDuffie; *Brit. Chem. Abs.* **B**, 1936, 438.

[115] F. Jacobsohn, British P. 427,777, 1935; *Chem. Abs.*, 1935, **29**, 6726; *J. Inst. Pet. Tech.*, 1935, **21**, 269A.

[116] E. B. McConnell, U. S. P. 1,950,900, Mar. 13, 1934, to Standard Oil Co. of Ohio; *Chem. Abs.*, 1934, **28**, 3580; *Brit. Chem. Abs.* **B**, 1935, 294.

[117] E. B. McConnell, U. S. P. 1,982,920, Dec. 4, 1934, to Standard Oil Co. of Ohio; *Chem. Abs.*, 1935, **29**, 598; *Brit. Chem. Abs.* **B**, 1936, 8; *J. Inst. Pet. Tech.*, 1935, **21**, 101A. U. S. P. 2,002,670, May 28, 1935; *Chem. Abs.*, 1935, **29**, 4934; *Brit. Chem. Abs.* **B**, 1936, 583.

[118] R. K. Stratford, Canadian P. 343,216, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1934, **28**, 7000.

[119] H. L. Allan, U. S. P. 1,990,466, Feb. 2, 1935, to Burmah Oil Co., Ltd.; *J. Inst. Pet. Tech.*, 1935, **21**, 176. British P. 407,522, 1934; *Chem. Abs.*, 1934, **28**, 5226; *Brit. Chem. Abs.* **B**, 1934, 532; *J. Inst. Pet. Tech.*, 1934, **20**, 335A.

[120] E. G. Ragatz, U. S. P. 2,029,504, Feb. 4, 1936, to Union Oil Co.; *Chem. Abs.*, 1936, **30**, 1994. *Cf.* C. P. McNeil, U. S. P. 2,046,081, June 30, 1936, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1936, **30**, 5784; *J. Inst. Pet. Tech.*, 1936, **22**, 410A.

[121] F. S. Dengler, E. W. Gardner and D. H. Felder, U. S. P. 2,024,096, Dec. 10, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 1226; *Brit. Chem. Abs.* **B**, 1936, 822. The use of antioxidants to retard excessive reaction in the manufacture of asphalts by oxidation of cracked residues is advocated by E. F. Nelson, U. S. P. 2,085,992, July 6, 1937, to Universal Oil Products Co.

[122] U. B. Bray and L. B. Beckwith, U. S. P. 1,988,715, Jan. 22, 1935, to Union Oil Co. of Calif.; *Chem. Abs.*, 1935, **29**, 1624; *Brit. Chem. Abs.* **B**, 1936, 85.

[123] U. B. Bray and L. B. Beckwith, U. S. P. 2,029,290, Feb. 4, 1935, to Union Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 1994.

[124] O. R. Douthett, U. S. P. 1,979,676, Nov. 6, 1933, to Barber Asphalt Co.; *Chem. Abs.*, 1934, **28**, 336; *Brit. Chem. Abs.* **B**, 1935, 936.

[125] O. R. Douthett, U. S. P. 1,976,677, Nov. 6, 1933, to Barber Asphalt Co.; *Chem. Abs.*, 1934, **28**, 336; *Brit. Chem. Abs.* **B**, 1935, 936. See also J. W. Sparks, U. S. P. 2,059,051, Oct. 27, 1936, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1937, **31**, 236.

[126] G. R. Hoover, U. S. P. 2,026,039, Dec. 31, 1935, to American Rolling Mill Co.; *Chem. Abs.*, 1936, **30**, 1226; *Brit. Chem. Abs.* **B**, 1936, 822; *J. Inst. Pet. Tech.*, 1936, **22**, 107A

portion of ammonia to the air for the purpose of reducing the olefin content and prolonging the adhesive life of the oxidized material.

PHYSICAL PROPERTIES OF PETROLEUM ASPHALTS

Possibly the more important characteristics of asphalts are their melting or softening points, penetration, viscosity and ductility.[126a] The softening point is determined generally by the ball and ring method. This comprises ascertaining the temperature at which a sample of asphalt, in a standard molded ring, will sag to a depth of 2.5 cm. under the weight of a small steel ball (of 0.375 in. diameter). A variation of this consists in placing 5 g. of mercury on a plug of asphalt (in a glass tube) and determining the temperature at which the mercury drops through the tube.[127]

Viscosity. The viscosity of an asphalt may be determined by any one of several methods,[128] including rate of flow through a capillary opening (Redwood, Saybolt or Ostwald viscosimeter), Couette rotating cylinder, and velocity with which a body of given weight sinks into the sample (e.g., Pochettino viscometer,[128a] previously mentioned). Traxler and Schweyer[129] found that this property was a linear function of the temperature between 15° and 35°C. and may be represented by the equation

$$\log\eta = at + \log b$$

in which η = viscosity in poises, T = temperature in °F., and a and n are constants. These investigators also suggest that the temperature susceptibility should be measured by the percentage decrease in viscosity for 1°C. temperature rise over this range. This value (also designated asphalt viscosity index or A.V.I.) may be calculated according to the formula

$$\text{A.V.I.} = 100[\eta_c/\eta_d(1/t_c - t_d) - 1]$$

in which η_c and η_d are the viscosities in poises at the temperatures t_c and t_d. Paraffin was is reported to lower the viscosity, and also adhesiveness, of asphaltic bitumen and the total quantity (including soft paraffin) should not exceed 5 per cent.[130]

Mitchell and Lee[131] call attention to the formula,

$$\eta T^n = a$$

in which η = viscosity in poises, T = temperature in °F., and a and n are constants. In its logarithmic form

$$\log\eta + n\log T = A$$

this indicates a straight line function between temperature and viscosity. Curves illustrating this linear relation are shown in Fig. 301 in which the logarithms of the temperature (°F.) are plotted against the logarithms of time of flow (in seconds) in a modified Ostwald viscosimeter.[132] Viscosity measurements at two, or better three, temperatures thus enable one to determine graphically the viscosity of the sample at any desired temperature. The slope of the line drawn through these points is equal to the value of *n*, and may be calculated according to the formula

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[126a] For details of the procedures for determining these values, see Handbook of Petroleum, Asphalt and Natural Gas, Kansas City Testing Laboratory, **1931**; A. S. T. M. Standards, American Society for Testing Materials, Philadelphia, **1933**. An investigation of the relationship between the physical properties of petroleum asphalts and their chemical composition has been made by J. Oberbach, "Über die Zusammensetzung von Erdölasphalten." Allgemeiner Industrie-Verlag, G.m.b.H., Berlin, **1936**. See also *J. Inst. Pet. Tech.*, 1937, **23**, 222A.

[127] G. Kraemer and C. Sarnov, *Chem. Ind.*, 1903, **26** (3), 55; *J.S.C.I.*, 1903, **22**, 291. Another modification of the ball and ring method has been proposed by Y. Uno and M. Ishida, *J.S.C.I., Japan*, 1935, **38**, Suppl. binding 658; *Chem. Abs.*, 1936, **30**, 2739.

[128] For descriptions and discussions of these procedures, see R. N. J. Saal, *Proceedings World Petroleum Congress, London*, 1933, **2**, 515; *Brit. Chem. Abs.* **B**, 1934, 913.

[128a] See. A. Pochettino, *Nuovo cimento*, 1914, **8**, 77. Also, C. Mack, *J. Phys. Chem.*, 1932, **36**, 2901.

[129] R. N. Traxler and H. E. Schweyer, *Physics*, 1936, 7, 67; *Chem. Abs.*, 1936, **30**, 3214; *J. Inst. Pet. Tech.*, 1936, **22**, 164A.

[130] Riehm, *Proc. World Petroleum Congr.*, 1933, **2**, 552; *Chem. Abs.*, 1935, **29**, 2726. See also J. Müller and D. Wandycz, *Przemysl Naftowy*, 1933, **8**, 361; *Chem. Abs.*, 1933, **27**, 5957. Increase of viscosity of asphalts on aging is discussed by R. N. Traxler and H. E. Schweyer, *Proc. Ann. Soc. Testing Materials*, 1936, **36**, 88; *Brit. Chem. Abs.* **B**, 1936, 991.

[131] J. G. Mitchell and A. R. Lee, *J.S.C.I.*, 1935, **54**, 407T.

$$n = \frac{\log\eta_1 - \log\eta_2}{\log T_2 - \log T_1}$$

in which η_1 and η_2 are viscosities in poises at temperatures (°F.) T_1 and T_2, respectively. This value *n* is also designated as the logarithmic temperature coefficient, and may be regarded as measure of susceptibility and is therefore a characteristic coefficient for the bitumen under consideration.

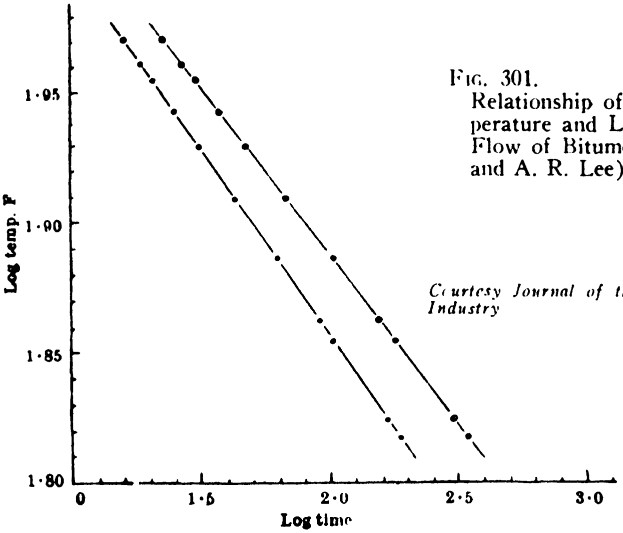

FIG. 301. Relationship of Logarithm of Temperature and Logarithm of Time of Flow of Bitumens. (J. G. Mitchell and A. R. Lee)

Courtesy Journal of the Society of Chemical Industry

Certain exceptions are tars having a low content of aromatics. In such instances the viscosity-temperature relation is represented by two intersecting straight lines, one for the lower temperature range and one for the upper. Such asphaltic bodies will, therefore, possess two logarithmic temperature coefficients, each characteristic over a particular temperature interval. An example of this is shown in Fig. 302.

Ductility. This is the distance (in cm.) which a briquette (of specified shape and dimensions) will stretch at 25°C. before breaking occurs, the rate of distention being 5 cm. per second. According to Müller and von Pilat[132a] asphaltene micelles are responsible for the very low ductility of some petroleum asphalts. This was indicated by the absence of these compounds in ductile asphalts, the increase in ductility (accompanied by increase in penetration) on their partial removal, and decreased ductility (and penetration) on their addition. Incorporation of an asphaltene solvent (e.g., naphthalene) increased ductility and penetration but lowered the softening point of asphalts, the optimum quantity being 7.5 per cent. Fulton and Kalichevsky[133] point out that blending tar resins substantially free of asphaltenes (and also oil) with low-grade asphalts improves the latter.

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[132] This instrument is described by A. R. Lee, *J.S.C.I.*, 1934, **53**, 69T.

[132a] J. Müller and S. von Pilat, *Asphalt Teer Strassenbautech.*, 1934, **34**, 649; *Chem. Abs.*, 1935, **29**, 6036; *Brit. Chem. Abs.* **B**, 1935, 535; *Chem. Zentr.*, 1934, **2**, 2929. For a discussion on the testing of asphalts, see A. R. Lee and A. H. D. Markwick, *J.S.C.I.*, 1937, **56**, 146T.

Penetration. This is the depth in one-hundredths of a centimeter to which a standard needle pierces the sample under specified conditions of time, temperature and weight. Generally the weight applied is 50, 100 or 200 g., depending upon the temperature. Holmes, Collins and Child[134] state that two methods have been employed for expressing the susceptibility factor, or change in consistency, of asphalts with the temperature:

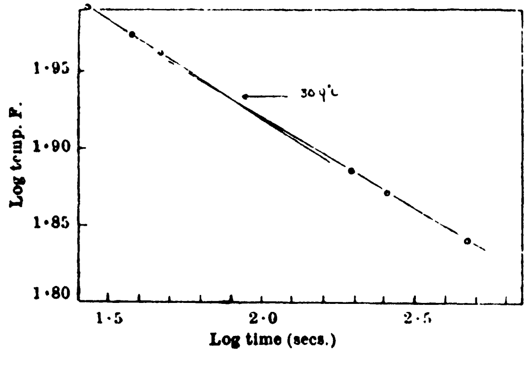

FIG. 302. Logarithmic Relationship of Temperature and Time of Flow for Tars of Low Aromatic Content. (J. G. Mitchell and A. R. Lee)

Courtesy Journal of the Society of Chemical Industry

$$\text{Susceptibility} = \frac{\text{penetration at } 46.1°\text{C.}/50 \text{ g.}/5 \text{ sec.} - \text{penetration at } 0°\text{C.}/200 \text{ g.}/60 \text{ sec.}}{\text{penetration at } 25°\text{C.}/100 \text{ g.}/5 \text{ sec.}} \quad (1)$$

$$\text{Susceptibility} = \frac{\text{penetration at } 37.8°\text{C.}/100 \text{ g.}/5 \text{ sec.}}{\text{penetration at } 25°\text{C.}/100 \text{ g.}/5 \text{ sec.}} \quad (2)$$

The first of these two, however, has been almost entirely supplanted by the second.

These investigators point out that no single method or factor has been developed which will serve to measure susceptibility over the desired range of consistency and temperature. They suggest three methods which can be used in conjunction with one another to give a fairly complete picture of the susceptibility characteristics of an asphalt.

Softening Point-Penetration Index. Correlation of data on the softening point and penetration of asphalts from a number of sources indicated that the following relation existed,

$$\log M = a \log P + \log k$$
$$\text{or } M = kP^a$$

in which M is the softening point (ball and ring) in °F., P is the penetration (at 25°C. per 100 g. per 5 sec.), and a and k are constants. Holmes, Collins and Child state that although the above relation gives no indication, by itself, of the change in consistency of an asphalt with temperature, nevertheless it is known (in a general manner) that the higher the penetration (at 25°C.) for a given softening point the less susceptible is the asphalt to temperature changes. To obtain more specific comparisons between different asphalts, a softening point-penetration index chart (Fig. 303) was developed, based on the same principle as that for a viscosity index chart for lubricating oils.[135] As standards, asphalt from heavy Mexican crude oil was chosen as 100 on the index scale and petroleum tar as 0. In the chart, the ordinates at the extreme left represent the penetrations (at 25°C. per 100 g. per 5 sec.) for petroleum tar and those on the heavy vertical line at 100 index for Mexican asphalt. Diagonal lines connecting these ordinates are the so-called iso-softening point lines. Thus, the straight line shown for 54.4°C. (130°F.) softening point is drawn between 19.5 and 57 penetration for petroleum tar and Mexican asphalt, respectively. The abscissas represent the index numbers.

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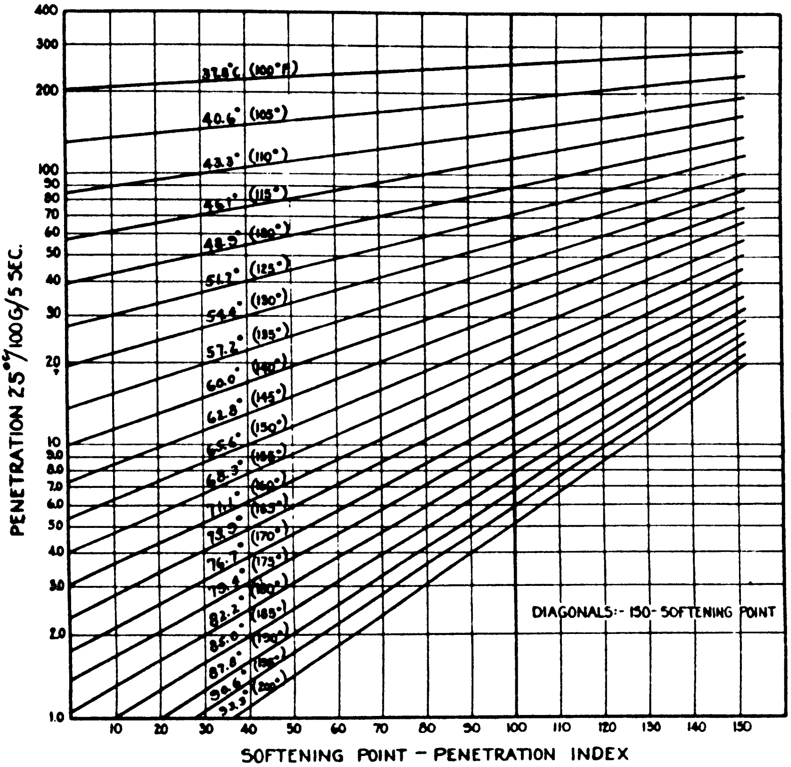
[133] S. C. Fulton and V. Kalichevsky, U. S. P. 1,926,523, Sept. 12, 1933, to Standard Oil Development Co.; *Brit. Chem. Abs.* **B**, 1934, 708.

[134] A. Holmes, J. O. Collins and W. C. Child, *Ind. Eng. Chem., Anal. Ed.*, 1936, **8**, 100; *Chem. Abs.*, 1936, **30**, 3996; *J. Inst. Pet. Tech.*, 1936, **22**, 320A; *Brit. Chem. Abs.* **B**, 1936, 531.



Courtesy Industrial and Engineering Chemistry

FIG. 303.—Softening Point — Penetration Index Chart for Asphalts. (A. Holmes, J. O. Collins and W. C. Child)

As an example of the use of this chart, it is desired to determine the softening point-penetration index of an asphalt having a softening point of 54.4°C. (130°F.) and 40 penetration at 25°C. per 100 g. per 5 seconds. The penetration is read on the ordinate scale, and the horizontal line at this point is followed until it intersects the 54.4°C. (130°F.) iso-softening point line. At this point the index number is read from the abscissa scale (vertically downward) giving a value of 67.

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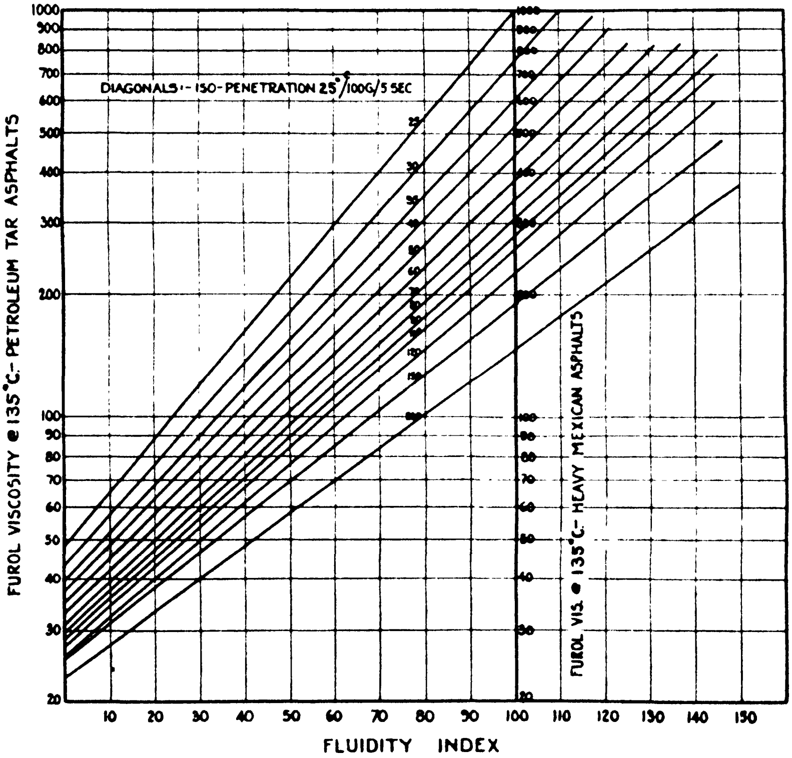
[135] For the viscosity index of lubricating oils, see E. W. Dean and G. H. Davis, *Chem. Met. Eng.*, 1929, 35, 618. Also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

Susceptibility Factor at Subnormal Temperatures. For temperatures below 25°C. (77°F.) the susceptibility factor may be expressed as:

$$\text{Susceptibility Factor} = \frac{\text{penetration at 25°C./100 g./5 sec.}}{\text{penetration at 0°C./200 g./60 sec.}}$$

The smaller the ratio of these two penetrations the lower, of course, is the change in consistency of the asphalt over this temperature range.



Courtesy Industrial and Engineering Chemistry

FIG. 304.—Chart for Fluidity Index of Asphalts. (A. Holmes, J. O. Collins and W. C. Child)

Fluidity Index. This was devised as a means of determining the susceptibility of asphalts at high temperature, and was developed in essentially the same manner as the softening point-penetration index except that the viscosity (seconds Furol) at 135°F. was substituted for the softening point. In the fluidity chart (Fig. 304) which can be employed in an analogous manner to the softening point-penetration chart, the ordinates are viscosity (Furol), the abscissas the fluidity index and the diagonal lines represent the penetration at 25°C. per 100 g. per 5 seconds.

An application of these three different values is shown by comparing the data (Table 225) obtained with asphalts having approximately the same penetration. For example, comparing Healdton and Colombian asphalts, it is seen that the former is less susceptible to normal temperature changes than Colombian, while the latter does not harden so rapidly (as indicated by the susceptibility factor) as Healdton at lower temperatures. Again, Mid-Continent and West Texas change in consistency to about the same degree at normal temperatures, but the former (as shown by fluidity index) is more readily affected by higher temperatures.[135a]

TABLE 225.—*Changes in Susceptibility Characteristics between Low and Elevated Temperatures*

Asphalt	Penetration at 25°C.	Softening Point-Penetration Index	Susceptibility Factor	Fluidity Index
Colombian	53	70	3.83	81
Healdton	55	73	6.11	—
Mid-Continent	50	63	3.92	85
West Texas	50	63	5.88	70

Pfeiffer and van Doormaal[136] report that the following relation

$$\log 800 - \log \text{penetration} = \alpha(t - 25°\text{C.})$$

exists between the penetration (25°C./100 g./5 sec.) and softening point (t) by the ball and ring method. The term α is characteristic of the susceptibility, and as it becomes greater or smaller the asphalt is designated as being correspondingly more or less sensitive to temperature change. To represent graphically the above relation and to furnish a means of classifying asphalts according to an index number, these investigators developed a nomogram (shown in Fig. 305) in which the ordinates are temperature and penetration and the diagonal represents the term α (or the susceptibility). Zero on the diagonal was chosen as the point at which the diagonal was intersected by a line connecting the softening point (40°C.) and penetration (200) for "not too heavy, steam refined Mexican bitumens." Division marks above and below the zero point were designated as + or —, respectively. A minus number indicated a high susceptibility index, a plus number the reverse.

According to this system, asphalts may be divided into three classes:

1. Those having an index between —1 and +1, and designated as the "N type" or normal asphalts. In this are included most steam refined bitumens generally used for road making.
2. Asphalts possessing an index number below —1 or the "Z type." These resemble coal-tar pitch in that they are characterized by great susceptibility and usually brittleness.
3. This class comprises bitumens exhibiting index numbers above +1, and are called the "R type." They possess low susceptibilities and only slight brittleness. The majority of blown-asphalts fall within this subdivision.

When asphalts are used in road construction, which constitutes their largest field of application, their efficiency as binding agents for stone and other mineral aggregates plays an important rôle. A study of the interfacial tensions between asphalts and solids has been made by Mack.[137] It was stated that when a liquid spreads over a solid surface two opposing forces are in play, one the adhesion of the liquid to the solid, and the other the cohesion of the liquid. The coefficient of

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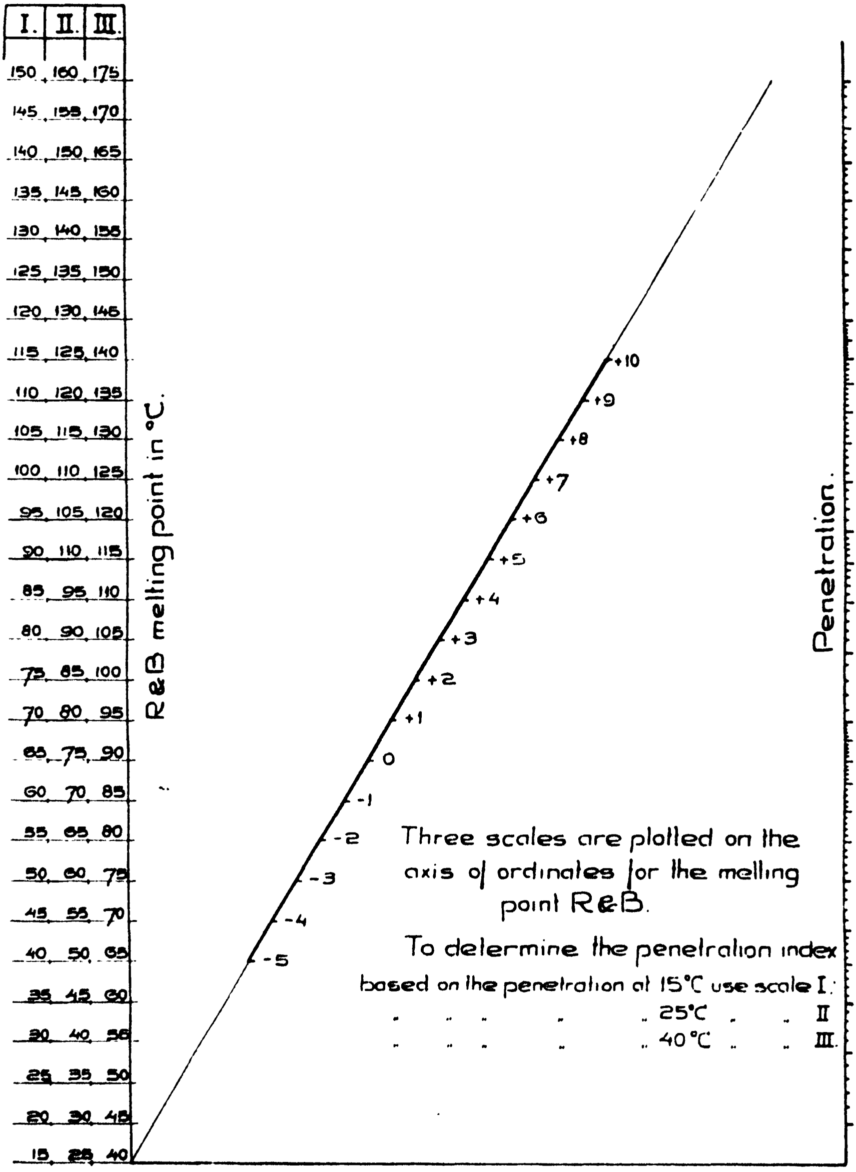
[135a] A discussion of penetration-temperature relationships is given by I. Bencowitz and E. S. Boe, *Ind. Eng. Chem., Anal Ed.*, 1936, **8**, 157; *Chem. Abs.*, 1936, **30**, 8592; *Brit. Chem. Abs.* **B**, 1936, 774; *J. Inst. Pet. Tech.*, 1936, **22**, 362A.

[136] J. P. Pfeiffer and P. M. van Doormaal, *J. Inst. Pet. Tech.*, 1936, **22**, 414; *Chem. Abs.*, 1936, **30**, 6545; *Brit. Chem. Abs.* **B**, 1936, 774; *J. Inst. Pet. Tech.*, 1936, **22**, 362A.

[137] C. Mack, *Ind. Eng. Chem.*, 1935, **27**, 1500; *Chem. Abs.*, 1936, **30**, 1201; *Brit. Chem. Abs.* **B**, 1936, 148; *J. Inst. Pet. Tech.*, 1936, **22**, 58A.



Three scales are plotted on the axis of ordinates for the melting point R&B.

To determine the penetration index based on the penetration at 15°C use scale I.
" " " " " 25°C " " II
" " " " " 40°C " " III.

Courtesy Journal of the Institution of Petroleum Technologists

FIG. 305.—Diagram for Determining Penetration Index. (J. P. Pfeiffer and P. M. van Doormaal)

spreading was defined as the energy of adhesion minus the energy of cohesion. Spreading occurs only if this coefficient is positive.[138] Asphalts having a high spreading coefficient toward a solid exhibit a high degree of wettability for that solid and give a thin film which leads to increased adhesivity.

The interfacial tension of asphalt and mineral aggregates was measured by determining the volume of powdered material, (200 mesh) which settled out of benzene solutions of the asphalts on standing after the two components were shaken. It was assumed that there is a straight-line relationship between the settling volume of powders in asphalt solutions and the concentration of the latter, and thus by extrapolation the value for the asphalt itself was computed. The interfacial tensions were found to vary with the type of aggregate and also with the type of asphalt. Low coefficients of spreading and low energies of adhesion were observed for the asphalts against silica and high values against limestone and blue clay.[139] Geissler[140] reports that the greatest adhesion for bitumens is shown by stones of a hydrophobic character. When the latter are hydrophylic in nature there is a tendency for water to penetrate between the stone and the bitumen layer.

Lee[141] also considered the problem of adhesion of bituminous materials to stones for road construction, particular attention being given to the effect of moisture present on the stones. It was assumed that the degree of wetting of a solid by a liquid will depend on the nature of the latter, its viscosity (which influences the rate of spreading), the character of the solid and the texture and cleanliness of the surface. Tests showed that the wetting properties of road tar on highly polished, water-moistened surfaces of stones were not influenced to any great extent by the type of stone employed. Differences in wetting tendencies were found to be the result of various degrees of roughness, water being presumably trapped in the minute crevices of a rough surface and preventing wetting of the solid by the binder.

USES OF PETROLEUM ASPHALTS

As stated previously the principal application of asphalt is in the construction of roads, acting as a binder for a filler of broken stone or sand or both.[142] Frequently asphalts are not used alone but are mixed with various proportions of tars and heavy oils to obtain a material best suited for the problem at hand.[143] Other uses include employment in roofing and flooring compositions and as coating material either alone or in paints and varnishes. An interesting application is in asphalt mattresses which are laid on the banks and beds of rivers to resist erosion by river currents.[144]

For altering the flowing qualities and hardness of asphalt compositions it has been proposed to add phenols,[145] fatty acids, soap and tetralin,[146] naphthalene,[147] bleaching earths[148] and paraffins and ceresin waxes.[149] Various molding compositions include asphalt mixed with such fillers as powdered quartz,[150] fuller's earth, talc or slate[151] and hydrated magnesium silicate.[152] A proposed wallboard material contains asphaltenes incorporated with cement and cotton or asbestos.[153] For the purpose of preservation, ropes may be impregnated with a solution of asphalt and rubber to which graphite has been added as a lubricant.[154] Steam-refined petroleum asphalt has been proposed as a final coating material for rubberized fabric, an intermediate layer of varnish being applied to impart flexibility.[155]

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[138] See also *Roads and Road Construction*, 1935, **13**, 77; *J. Inst. Pet. Tech.*, 1935, **21**, 227A.

[139] For a general discussion of admixtures of asphaltic products and mineral aggregates, see P. Hubbard, *Proc. World Petroleum Congr.*, 1933, **2**, 601; *Chem. Abs.*, 1934, **28**, 4895; *Brit. Chem. Abs.* **B**, 1934, 661.

[140] W. Geissler, *Bitumen*, 1934, **4**, 191; *Chem. Abs.*, 1936, **30**, 3196; *J. Inst. Pet. Tech.*, 1934, **20**, 612A. W. Geissler and H. Kleinert, *Asphalt Teer Strassenbautech.*, 1936, **36**, 481; *J. Inst. Pet. Tech.*, 1936, **22**, 461A; *Chem. Abs.*, 1936, **30**, 6528.

[141] A. R. Lee, *J.S.C.I.*, 1936, **55**, 23T; *Chem. Abs.*, 1936, **30**, 2722; *J. Inst. Pet. Tech.*, 1936, **22**, 220A.

[142] For an extended discussion of this subject see P. E. Spielmann and A. C. Hughes, "Asphalt Roads," Edward Arnold & Co., London, **1936**. See also D. M. Wilson, *Chemistry and Industry*, **1934**, 924; *J. Inst. Pet. Tech.*, 1934, **20**, 624A; *Chem. Abs.*, 1935, **29**, 1603. Road asphalt specifications are considered in *Nat. Pet. News*, 1936, **28** (31), **24B**.

[143] See F. Macht, *Proc. World Petroleum Congr., London*, 1933, **2**, 581; *Brit. Chem. Abs.* **B**, 1934, 661. The significance of viscosity of road tars is discussed by G. H. Fuidge, *Chemistry and Industry*, **1936**, 301; *J. Inst. Pet. Tech.*, 1936, **22**, 321A; *Brit. Chem. Abs.* **B**, 1936, 581; *Chem. Abs.*, 1936, **30**, 4294; *Asphalt Teer Strassenbautech*, 1936, **36**, 595; *Chem. Abs.*, 1936, **30**, 8557. G. Barr, *Chemistry and Industry*, **1936**, 576; *Chem. Abs.*, 1936, **30**, 6924.

[144] See C. O. Willson, *Oil and Gas. J.*, 1934, **33**, (16), 20; *J. Inst. Pet. Tech*, 1934, **20**, 625A. W. C. Carey, *Information Series Asphalt Institute*, **1936**, No. 25.

ASPHALT EMULSIONS

Usual procedures for the application of asphalt as a protective coating consist in either heating until it becomes fluid and then applying in a molten condition or effecting a suspension in organic liquids (so-called "cutbacks"), e.g., naphtha, and brushing or spraying such compositions on surfaces to be covered. Later developments, however, comprise the preparation of aqueous emulsions of asphalts, usually with the aid of some emulsifying agent, followed by spreading such emulsions on the surfaces to be coated.[156] After evaporation of the water, the residual film is irreversible, i.e., will not re-emulsify when placed in water. Also it is ductile and resistant to flow under heat, this latter property being attributed to a gel or honeycomb structure.

According to Ross,[157] the proportions of ingredients may vary over a wide range, representative limits being 45 to 75 per cent asphalt, 25 to 55 per cent water, and 1 to 10 per cent emulsifying agent. However, as extreme examples as low as 30 per cent and as high as 95 per cent asphalt have been employed. As a rule the bitumens possess softening points of 110° to 160°F. and penetrations of 35 to 200 (at 77°F.). In this connection it is interesting to note that flowable compositions having 80 to 85 per cent of the asphalt have been reported.[158] One mode of procedure is first to make an aqueous emulsion containing about 57 per cent bitumen, the average particle size of the latter being about 2 microns. Additional bitumen is then incorporated, mechanical agitation during this latter step being less severe than in the first stage and resulting in the formation of dispersed particles of about 20 to 30 microns in size.

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[145] E. Roualt, British P. 421,113, 1934; *Brit. Chem. Abs.* **B**, 1935, 260; *Chem. Abs.*, 1935, **29**, 3824.

[146] O. Smiley, U. S. P. 2,005,113, June 18, 1935; *Chem. Abs.*, 1935, **29**, 5248; *Brit. Chem. Abs.* **B**, 1936, 629.

[147] German P. 623,401, 1935, to Chem. Fabr. Flörsheim H. Noerdlinger A.-G.; *Chem. Abs.*, 1936, **30**, 2346.

[148] A. Wolf, British P. 424,415, 1935, to R. Herrmann, Ltd.; *Brit. Chem. Abs.* **B**, 1935, 538; *Chem. Abs.*, 1935, **29**, 5650; *J. Inst. Pet. Tech.*, 1935, **21**, 176A.

[149] M. M. Faingar and E. M. Braudo, *Neft. Khoz.*, 1935, **28** (3), 67; *Chem. Abs.*, 1936, **30**, 3996; *J. Inst. Pet. Tech.*, 1936, **22**, 164A.

[150] E. Graefe, *Petroleum Z.*, 1935, **31** (40), 1; *Chem. Abs.*, 1936, **30**, 2740; *Bitumen*, 1935, **5**, 54; *Chem. Zentr.*, 1935, **2**, 161; *Brit. Chem. Abs.* **B**, 1936, 774. For a discussion of the uses of bitumen plastics see C. G. F. Pritchett, *Chemistry and Industry*, **1937**, 543.

[151] E. W. Gardner and D. H. Felder U. S. P. 2,045,906, June 30, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 5784.

[152] W. A. Craig and F. E. Griffith, U. S. P. 1,997,569, April 16, 1935, to Richfield Oil Co. of Calif.; *Chem. Abs.*, 1935, **29**, 3824

[153] S. C. Fulton and V. Kalichevsky, U. S. P. 2,035,122, Mar. 24, 1936, to Standard Oil Development Co.; *Chem. Abs.*, 1936, **30**, 3132.

[154] L. M. Madsen, Danish P. 50,907, 1935; *Chem. Abs.*, 1936, **30**, 5430

[155] J. R. Couture U. S. P. 1,936,500, Nov. 21, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, **28**, 914; *Brit. Chem. Abs.* **B**, 1934, 797.

[156] For a general discussion of asphalt emulsions, see L. Kirschbaum, *Chem. Met. Eng.*, 1929, **36**, 477. E. H. Kadmer, *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 225; *Chem. Abs.*, 1935, **29**, 8309; *Asphalt u. Teer*, 1935, **35**, 167; *J. Inst. Pet. Tech.*, 1935, **21**, 163A. G. D. Kreitzer and K. M. Bekreneva, *Narod. Komissariat, Tyaz. Prom. U.S.S.R., Leningrad, Plastmassui*, 1935, 1, 342; *Chem. Abs.*, 1936, **30**, 2740.

[157] E. S. Ross, *J.S.C.I.*, 1929, **48**, 112T

[158] A. G. Terry, L. G. Gabriel and J. F. T. Blott, U. S. P. 2,009,821, July 30, 1935; *Chem. Abs.*, 1935, **29**, 6420.

Factors which affect the stability of such emulsions are: presence of some types of electrolytes in the water,[159] hydrogen-ion concentration of the latter, degree of dispersion of the asphalt, and the interfacial tension between the dispersed phase and the aqueous medium. With regard to the hydrogen-ion concentration, Vellinger and Flavigny[160] report that greatest stability (of a 50 per cent asphalt emulsion containing soap as the emulsifying agent) was secured over a *p*H range of 9 to 13. The latter was measured with an antimony electrode. They also point out that the interfacial tension between the dispersed particles and the liquid medium should be as low as possible. Gräfe and Fleck[161] call attention to the undesirability of an extremely fine dispersion since in this manner the total quantity of emulsifier absorbed by the particles is increased. This results in an asphalt film (particularly when the emulsion is applied to road surfaces) which exhibits a tendency to re-emulsify due to the combined action of moisture and traffic.

The interfacial tensions of two asphalts (Fluxes A and B) against aqueous sodium hydroxide, at 85°C., were measured by Traxler and Pittman.[162] The samples employed exhibited the following physical properties:

	Flux A	Flux B
Sp.gr. 85°/85C.	0.9964	0.9970
Float at 150°F., seconds[a]	44	53
Flash (Cleveland Open Cup), °F.	420	415

[a] Time required for water (at a specified temperature) to force a plug of asphalt out of the bottom of a saucer-like aluminum float, thereby causing the latter to sink. For details, see A.S.T.M. Standards, American Society for Testing Materials, Philadelphia, Pa., 1933.

These investigators found that the interfacial tension decreased with increasing concentration of alkali, disappearing when the latter became 0.05 and 0.005 moles per liter for Fluxes A and B, respectively. Some of their results are given in Table 226.

TABLE 226.—*Interfacial Tension between Asphaltic Fluxes and Solutions of Sodium Hydroxide.*

Concentration of NaOH Moles per Liter	Interfacial Tension Flux A Dynes per cm.	Interfacial Tension Flux B Dynes per cm.
0.0000	16.7	15.7
0.0013	11.4	7.9
0.0025	9.5	5.3
0.0050	5.3	0.0[a]
0.0100	0.5	0.0
0.0500	0.0[a]	0.0

[a] Emulsion-formation at the interface apparently occurred with this concentration, and greater, of alkali.

The effect of sodium chloride, in small proportions, was to decrease the interfacial tension of asphalts against aqueous alkali. As the proportion of salt was increased, however, the opposite phenomenon was observed. This is illustrated graphically in Fig. 306 by the data obtained with Flux A and 0.0050 molar sodium hydroxide and Flux B and 0.0025 molar alkali. Substitution of calcium chloride for salt resulted only in increasing the tension.

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[159] Hard water, for example, before being employed in the preparation of asphalt emulsions, may be softened by treatment with alkali fluorides: K. E. McConnaughay, U. S. P. 1,989,374, Jan. 29, 1935; *Brit. Chem. Abs.* **B**, 1935, 1083.

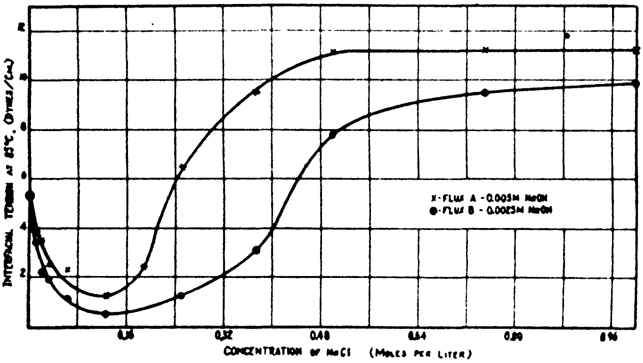
[160] E. Vellinger and B. Flavigny, *Ann. combustibles liquides*, 1932, 7, 217; *Chem. Abs.*, 1932, **26**, 5473.

[161] F. H. Gräfe and I. R. Fleck, *Petroleum*, 1930, **26**, 357; *Brit. Chem. Abs.* **B**, 1930, 542.

[162] R. N. Traxler and C. U. Pittman, *Ind. Eng. Chem.*, 1932, **24**, 1003.

Salts, e.g., sodium borate, carbonate, phosphate or silicate, which yield alkaline aqueous solutions because of hydrolysis, may be employed in place of alkali. With such compounds, however, the concentration required to reduce the interfacial tension to zero varies considerably and is probably dependent not only on the alkalinity of the solution (or degree of hydrolysis) but also on the type of anion present.[163]

Traxler[164] states that the viscosity of aqueous bitumen emulsions is influenced by both the particle size and the particle-size uniformity of the disperse phase, the latter factor being the more important. With a constant phase-volume ratio a decrease in particle size causes a rise in consistency. On the other hand if the particles are not of uniform size there is a decrease in consistency because of the resultant condition of more loose packing with non-uniform than with uniform particles.



Courtesy Industrial and Engineering Chemistry

FIG. 306.—Effect of Sodium Chloride on Interfacial Tension Between Sodium Hydroxide Solutions and Asphalts. (R. N. Traxler and C. U. Pittman)

PREPARATION OF ASPHALT EMULSIONS

As previously indicated, such emulsions may be prepared by dispersing asphalt (for example, by mechanical agitation) in an aqueous solution of an emulsifying agent. Of the latter the sodium salts of fatty acids are probably the best known and have been widely employed. In some instances these may be used in conjunction with heavy metal soaps. As an illustration, Hepburn[164a] suggests making an emulsion of 9 parts of soap, 78 parts of water and 20 parts of fuel oil. This is mixed with 1 to 2 parts of aluminum oleate and 296 parts of asphalt then dispersed in the composition. In other cases substances which react to form soaps may be employed. Thus, bone fat may be heated with aqueous potassium carbonate and then molten bitumen incorporated.[165] Or stearine pitch (2 to 5 per cent) is dissolved in asphalt and the latter dispersed in a dilute solution of sodium hydroxide.[166]

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[163] R. N. Traxler and C. U. Pittman, *Ind. Eng. Chem.*, 1932, **24**, 1391.

[164] R. N. Traxler, *Ind. Eng. Chem.*, 1936, **28**, 1013; *Brit. Chem. Abs.* **B**, 1936, 1075; *J. Inst. Pet. Tech.*, 1936, **22**, 461A; *Chem. Abs.*, 1936, **30**, 7417.

[164a] D. McK. Hepburn, U. S. P. 1,931,072, Oct. 17, 1933, to Amiesite Asphalt Co. of America; *Brit. Chem. Abs.* **B**, 1934, 747.

[165] British P. 276,543, 1926, to Mineral A.-G. Brig; *Brit. Chem. Abs.* **B**, 1927, 836.

Alkali rosinates may be substituted for the corresponding fatty acid derivatives.[167] Gabriel and Blott[168] recommend that emulsions prepared with such rosinates be stabilized by incorporation of calcium, or other water-insoluble, salts of rosin. As an illustration, 100 parts of rosin and 3.75 parts of calcium hydroxide are heated at 140°C. until a homogeneous mass is obtained. The latter is dissolved in an equal weight of fuel oil and 4 parts of this solution are added to 100 parts of bitumen. The resulting mixture is dispersed in sufficient aqueous 0.05N potassium rosinate to give an emulsion containing 57 per cent bitumen. Certain esters of abietic or hydroabietic acid have also been recommended, such as those prepared by esterifying in an alkaline medium with a halogeno-aliphatic sulphonic acid or in an acid medium with a hydroxyaliphatic sulphonic acid.[169]

In some instances crude petroleums contain naturally occurring emulsifiers. These may be recovered in the following manner:[170] The crude oil is distilled taking over gasoline, kerosene and the lubricating oil fractions. Alkali, e.g., sodium or potassium hydroxide, is added to the last-named fractions and these are again distilled. In the resulting residue are found the emulsifiers combined with the alkali. The residue may be added directly to the bitumen or it may be treated with an acid (hydrochloric or sulphuric) and the emulsifiers thus liberated be incorporated with the asphaltic material.

As previously mentioned, inorganic alkalies or salts yielding alkaline aqueous solutions may serve as the emulsifying agent. A typical salt is sodium metasilicate.[171] Ernotte[172] suggests the muds resulting from the carbonating of sugar juices as dispersing and peptizing media. Such "carbonating muds" or "sugar scum" are said to contain, in addition to calcium carbonate, colloidal calcium salts such as the pectate. A mixture of slaked lime and alum has also been suggested.[173]

The use of inorganic salts in conjunction with soaps of various types has been recommended, particularly in the preparation of emulsions possessing a high percentage of asphalt. Thus, in preparing a composition containing 1 part of water and 2 parts of asphalt, Steininger[174] uses about 1 per cent of triethanolamine oleate and 1.5 per cent of sodium sulphite or chromate. Sparks[175] employs a small proportion of a mixture of sodium silicate or phosphate and "green acid soap." The latter is derived from the water-soluble sulphonic acids found in acid sludge from the refining of petroleum distillates.[176] In another procedure trisodium phosphate

[166] O. F. Neitzke, U. S. P. 1,981,522, Nov. 20, 1934; *Brit. Chem. Abs.* **B**, 1935, 1083.

[167] See for example, D. N. Meyers, U. S. P. 1,957,031, May 1, 1934; *Brit. Chem. Abs.* **B**, 1935, 214. J. B. Small, U. S. P. 2,027,404, Jan. 14, 1936, to Glidden Co.; *Chem. Abs.*, 1936, **30**, 1556. O. F. Neitzke, U. S. P. 1,940,432, Dec. 19, 1933, to Bennett Inc.; *Brit. Chem. Abs.* **B**, 1934, 917. J. Miscall, U. S. P. 2,053,099, Sept. 1, 1936, to Patent and Licensing Corp.; *Chem. Abs.*, 1936, **30**, 7328. Plant-scale manufacture of this type of emulsion is described by J. W. Smith, *Refiner*, 1936, **15**, 306; *J. Inst. Pet. Tech.*, 1936, **22**, 513A.

[168] L. G. Gabriel and J. F. T. Blott, British P. 441,782, 1936, to Colas Products Ltd.; *Chem. Abs.*, 1936, **30**, 4665. *Cf.* French P. 792,874, 1936, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1936, **30**, 4316. Also Australian P. 23,721, 1936, to Asphalt Cold Mix (Australia) Pty. Ltd.; *Chem. Abs.*, 1936, **30**, 6552.

[169] British P. 425,217, 1935, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* **B**, 1935, 443; *Chem. Abs.*, 1935, **29**, 5546; *J. Inst. Pet. Tech.*, 1935, **21**, 222A.

[170] H. Limburg, U. S. P. 1,915,062, June 20, 1933, to Flintkote Corp.; *Brit. Chem. Abs.* **B**, 1934, 311.

[171] P. R. Smith, U. S. P. 1,989,775, Feb. 5, 1935, to Barber Asphalt Co.; *Chem. Abs.*, 1935, **29**, 1980.

[172] M. Ernotte, British P. 428,908, 1935; *J. Inst. Pet. Tech.*, 1935, **21**, 312A.

[173] D. Finley, U. S. P. 1,625,304, April 19, 1927; *Chem. Abs.*, 1927, **21**, 2060; *Brit. Chem. Abs.* **B**, 1927, 403.

[174] H. M. Steininger, U. S. P. 1,988,879, Jan. 22, 1935, to Standard Oil Co. of Ind.; *Brit. Chem. Abs.* **B**, 1936, 85.

[175] J. W. Sparks, U. S. P. 1,956,779, May 1, 1934, to Standard Oil Co. of Ind.; *Brit. Chem. Abs.* **B**, 1935, 294.

[176] For the isolation of such sulphonic acids and their corresponding soaps, see Chapter 46. Also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

or caustic alkali serves as the dispersing agent.[177] After emulsification, the composition is incorporated with a small quantity of tannic acid.

Other substances which have been proposed as emulsifying agents are humic acid,[178] rosin soaps,[179] alkali-metal or ammonium salts of oleyl, cetyl or stearyl sulphate,[180] and viscose.[181] Compositions containing humic acid are said to be stabilized by incorporation of a small proportion (0.5 to 1 per cent) of a neutral salt, such as sodium chloride or sulphate or calcium chloride.[182] Taylor[183] uses farinaceous materials, such as corn (maize), gluten or soya-bean meal, mixed with water-soluble soaps of petroleum sulphonic acids (green acid soap). Such an agent furnishes asphalt emulsions which may be diluted with hard water or subjected to wide variations in temperature without breaking. Starchy bodies, such as flour rendered water-soluble by treatment with alkali, incorporated with alkali phenylates or fatty acid soaps, are recommended by Rouault.[184] Before emulsification, the viscosity of the bitumen may be decreased by incorporating phenols (or phenylates) with it.[185]

In addition to emulsifying agents, substances whose functions are to stabilize or prevent the emulsion from breaking rapidly may be included also. To accomplish this Watts[186] suggests employment of an alkali metal caseinate. Afterwards phosphoric or boric acid is added until the *p*H of the composition is 8.5. In addition, a preservative for the casein, such as formaldehyde, may be used. In using sodium caseinate, Bray and Beckwith[187] suggest that the emulsion be prepared and then cooled below 38°C. before incorporating the stabilizer. Sodium phosphate has been recommended as a stabilizer for emulsions prepared with alkali or with soap as emulsifying agent.[188] In the latter case a small percentage of calcium chloride is also incorporated. Thurston[189] points out that spent fuller's earth from the vapor-phase treatment of cracked distillates contains adsorbed saponifiable bodies. Extraction of the latter with acetone or benzene furnishes substances which possess stabilizing properties. Wintsch[190] recommends mixing 5 to 10 per cent rubber latex with a 2 per cent solution of rosin soap which is then emulsified with the bitumen. Water- or alkali-soluble condensation products of formaldehyde and phenols have been proposed also.[191] In other instances the bitumen, prior to emulsification, may be mixed with sulphurized factice, such as obtained by the

[177] A. L. Halvorsen, U. S. P. 1,995,346, Mar. 26, 1935; *Chem. Abs.*, 1935, **29**, 3151.

[178] British P. 433,550, 1934, to I. G. Farbenind. A.-G ; *Brit. Chem. Abs.* **B**, 1935, 1083. See also, H. Klein, U. S. P. 2,038,572, April 28, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 4004.

[179] J. C. Roediger, U. S. P. 1,988,336, Jan. 15, 1935, to Patent and Licensing Corp.; *Brit. Chem. Abs.* **B**, 1936, 53.

[180] British P. 437,674, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1936, **30**, 2749.

[181] H. Levin, U. S. P. 1,997,868, Apr. 16, 1935, to Patent and Licensing Corp.; *Chem. Abs.*, 1935, **29**, 3752; *Brit. Chem. Abs.* **B**, 1936, 442.

[182] K. Daimler, German P. 627,465, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1936, **30**, 4316. British P. 430,917, 1933; *Brit. Chem. Abs.* **B**, 1935, 891.

[183] K. Taylor, U. S. P. 1,932,648, Oct. 31, 1933, to Standard Oil Co. of Ind.; *Brit. Chem. Abs.* **B**, 1934, 822.

[184] E. Rouault, French P. 748,886, 1933; *Chem. Abs.*, 1933, **27**, 5531. British P. 419,358, 1933; *Brit. Chem. Abs.* **B**, 1935, 88; *Chem. Abs.*, 1935, **29**, 2736. See also, French P. 748,893 and 748,894, 1933; *Chem. Abs.*, 1933, **27**, 5532.

[185] E. Rouault, British P. 421,113, 1934; *Chem. Abs.*, 1935, **29**, 3824.

[186] V. E. Watts, U. S. P. 2,040,115, May 12, 1936, to American Bitumuls Co.; *Chem. Abs.*, 1936, **30**, 4664.

[187] U. B. Bray and L. B. Beckwith, U. S. P. 2,022,229, Nov. 26, 1935, to Union Oil Co. of Calif.; *Chem. Abs.*, 1936, **30**, 837; *Brit. Chem. Abs.* **B**, 1936, 777.

[188] British P. 427,720, 1935, to International Bitumen Emulsions Corp.; *Brit. Chem. Abs.* **B**, 1935, 662; *Chem. Abs.*, 1935, **29**, 6420.

[189] R. k. Thurston, U. S. P. 2,037,669, Apr. 14, 1936, to Texas Co.; *Chem. Abs.*, 1936, **30**, 4004.

[190] V. Wintsch, Jr., French P. 648,917, 1928; *Chem. Zentr.*, 1929, **2**, 100; *Chem. Abs.*, 1929, **23**, 3069.

[191] German P. 602,165, 1934, to J. R. Geigy A.-G.; *Chem. Abs.*, 1935, **29**, 598. French P. 781,331, 1935; *Chem. Abs.*, 1935, **29**, 6420. British P. 438,162, 1934; *Brit. Chem. Abs.* **B**, 1936, 180. *Cf.* W. Reiner, German P. 611,491, 1935; *Chem. Abs.*, 1935, **29**, 4160.

action of sulphur chloride on train oil or fatty acids or by heating linseed oil and sulphur to 150-180°C.[192]

Hickman[193] suggested an emulsion made by dispersing bitumen in an alkaline solution of casein to which had been added rosin or a sulphonated fatty oil and a small percentage of acetanilide or salicylic acid. To obtain a stable emulsion of extremely small particle size it is necessary that the alkalinity of the dispersing medium be adjusted so that it is slightly less than the critical point above which a water-in-oil emulsion would be formed.[194]

Use of Clay in Asphalt Emulsions. According to Fain,[195] asphalt emulsions may be classified in two ways: (a) those containing a surface tension depressor, such as soap, and are easily and readily prepared, and (b) those possessing an insoluble dispersing agent such as clay or bentonite. In the latter instance careful regulation of the temperature and viscosity of the dispersing medium during manufacture is necessary. The latter type, however, is generally more stable toward electrolytes and during storage. He proposes to combine both of these effects, stability and ease of preparation, by incorporating both kinds of agents. A typical composition would contain approximately 75 per cent asphalt, 25 per cent water, 0.5 per cent bentonite and 1/16 per cent soap. In some instances the soap may be substituted by a small proportion (0.025 to 0.1 per cent) of a protective colloid. Examples of the latter are gum acacia, agar agar, starch and tannic acid.[196] As a modification, Kirschbraun[197] suggests that an aqueous emulsion containing asphalt (about 70 per cent) and soap be mixed with one (55-60 per cent asphalt) having clay as the stabilizing substance. The resulting product is said to be more fluid than either of the component emulsions. It has been pointed out also that the *p*H value of compositions of which clay is one constituent should be from 6 to 9.[198] For example, steam-refined Mexican asphalt (melting at 120°F.) may be emulsified with an aqueous suspension of bentonite and clay provided the *p*H value of the dispersion is 6.0 to 6.5. On the other hand the optimum emulsive condition for certain pitches (e.g., stearine) exists at a *p*H of about 8.0. Since various clays furnish aqueous suspensions differing greatly in their acidity or alkalinity, incorporation of a small proportion of a modifying agent (such as alum, sulphuric acid, or alkali metal oxides or hydroxides) is often necessary to secure effective dispersion of the asphalt or pitch.

Another procedure comprises emulsifying molten asphalt with 1 to 5 per cent of a concentrated solution of an alkali hydroxide or carbonate and then incorporating an aqueous slurry of clay.[199] The latter material, according to Liberthson,[200] may be employed in small proportions to stabilize bituminous compositions containing petroleum sulphonates as emulsifying agents. Increased fluidity is said to result on the addition of trisodium phosphate to preparations composed of asphalt, clay and aqueous alkali.[201] If soap be used in place of the alkali, then addition of the phosphate should be preceded by that of an alkaline-earth metal salt, such as calcium chloride. Lister[202] recommends an alkaline aqueous suspension of bentonite and sodium or potassium silicate as stabilization agents. Emulsification of bitumen in an aqueous colloidal solution of hydrated magnesium silicate with the aid of 0.1N acetic acid has also been suggested.[203]

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[192] British P. 271,177, 1926, to Mineral A.-G. Brig.; *Brit. Chem. Abs.* **B**, 1927, 595; *Chem. Abs.*, 1928, **22**, 1677.

[193] T. M. Hickman, British P. 308,389, 1929; *Brit. Chem. Abs.* **B**, 1929, 434.

[194] P. R. Smith and O. R. Douthett, U. S. P. 1,994,542, March 19, 1935, to Barber Asphalt Co.; *Chem. Abs.*, 1935, **29**, 3152; *Brit. Chem. Abs.* **B**, 1936, 357.

[195] J. M. Fain, U. S. P. 1,793,918, Feb. 24, 1931, to Flintkote Co.; *Brit. Chem. Abs.* **B**, 1931, 960; *Chem. Abs.*, 1931, **25**, 2281. Also, J. M. Fain, U. S. P. 2,027,582, Jan. 14, 1936, to Patent and Licensing Corp.; *Chem. Abs.*, 1936, **30**, 1556.

[196] L. Kirschbraun, U. S. P. 1,869,697, Aug. 2, 1932, to Flintkote Corp.; *Chem. Abs.*, 1932, **26**, 5413; *Brit. Chem. Abs.* **B**, 1933, 499.

[197] L. Kirschbraun, U. S. P. 1,948,881, Feb. 27, 1934, to Patent and Licensing Corp.; *Chem. Abs.*, 1934, **28**, 2870; *Brit. Chem. Abs.* **B**, 1934, 999.

[198] L. Kirschbraun and H. L. Levin, U. S. P. 1,960,112, May 22, 1934, to Patent and Licensing Corp.; *Brit. Chem. Abs.* **B**, 1935, 295. British P. 321,721, 1928, to Flintkote Co.; *Chem. Abs.*, 1930, **24**, 2877.

[199] German P. 601,891, 1934, to Firma Paul Lechler; *Chem. Abs.*, 1934, **28**, 7520.

[200] L. Liberthson, U. S. P. 1,940,807, Dec. 26, 1933, to L. Sonneborn Sons, Inc.; *Brit. Chem. Abs.* **B**, 1934, 868.

USES OF ASPHALT EMULSIONS

The advantages of using emulsions over other methods of applying asphalt coatings have already been pointed out to some extent. Employment of asphalt alone requires heating to a high temperature which may be disadvantageous in some cases. However, asphalt solutions to be brushed or sprayed may introduce fire and health hazards. Among the numerous applications[203a] are in the making of roads, flooring and roofing, in the waterproofing of paper, cloth, wood and concrete and the manufacture of molded material by mixture with various fillers. An important use is in applying protective coating for iron and steel. Treatment of surface soil with bituminous emulsions is said to minimize dust-formation in dry weather and mud in wet weather.[204] A lubricant for bearing surfaces to be subjected to high temperatures consists of an aqueous emulsion of asphalt and graphite.[205]

TESTING OF ASPHALT EMULSIONS

According to Latzko,[206] such emulsions may be divided into three main classes, (a) normally breaking, (b) slowly breaking, and (c) stable. The first-named types, generally containing 45-50 per cent water, are used in road construction, particularly with limestone aggregates, since the bitumen particles are more adherent to this. Stable emulsions are especially applicable for mixing with stone, sand, and other finely-divided material to form an asphalt concrete. Klingmann[207] believes that breaking can be traced mainly to precipitation of the soap in the emulsion by the soluble constituents of the aggregate.[208] However, filtration and evaporation are also factors. As the purpose of bituminous emulsions, in road making, is to envelop the aggregate uniformly with a binding material, any premature breaking will result in irregularities. He suggests as a test that asphalt composition be allowed to flow upwards through a glass tube, packed with aggregate 1 mm. in diameter, and the volume noted which enters the tube before the top surface of the liquid breaks. The latter phenomenon is indicated by a cessation of liquid flow.

Weber[209] proposes covering 10 g. of clean, dried stone (0.6 to 2 mm. diameter) with 50 cc. of the emulsion and allowing the mixture to stand for 1 hour. Afterwards the stone is washed with water to remove excess asphalt, dried, and the increase in weight determined. McKesson[210] describes a breaking test in which 100 g. of the emulsion are stirred with 35 cc. of $0.02N$ calcium chloride. After 2 minutes, precipitated asphalt is filtered, dried at 163°C. and weighed. With slow settling compositions a $0.1N$ solution may be employed.

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[201] British P. 427,720, 1935, to International Bitumen Emulsions Corp.; *Chem. Abs.*, 1935, **29**, 6420.

[202] F. V. Lister, British P. 436,494, 1935; *Chem. Abs.*, 1936, **30**, 1994.

[203] R. K. Painter, H. H. Moreton and C. W. Hill, U. S. P. 2,023,540, Dec. 10, 1935; *Chem. Abs.*, 1936, **30**, 852; *Brit. Chem. Abs.* **B**, 1936, 969.

[203a] L. Kirschbraun, *Chem. Met. Eng.*, 1929, **36**, 477; *Chem. Abs.*, 1929, **23**, 4812. J. M. Fain and F. D. Snell, *Paint, Oil, Chem. Rev.*, 1936, **98** (13), 14; *Chem. Abs.*, 1936, **30**, 8650; *Brit. Chem. Abs.* **B**, 1936, 1005.

[204] C. H. Haswell, *Paint Technology*, 1936, 1, 142; *Brit. Chem. Abs.* **B**, 1936, 696.

[205] M. J. Heitmann, U. S. P. 1,984,214, Dec. 11, 1934, to Patent and Licensing Corp.; *Chem. Abs.*, 1935, **29**, 922; *Brit. Chem. Abs.* **B**, 1935, 984.

[206] W. Latzko, *Petroleum Z.*, 1935, **31** (11), 4; *Chem. Abs.*, 1935, **29**, 7061. See also W. Geissler and H. Kleinert, *Asphalt Teer Strassenbautech.*, 1935, **35**, 1019, 1038; *Chem. Abs.*, 1936, **30**, 3961; *Brit. Chem. Abs.* **B**, 1936, 596.

[207] G. H. Klingmann, *Bitumen*, 1935, **5**, 206; *Chem. Abs.*, 1936, **30**, 2740; *J. Inst. Pet. Tech.*, 1936, **22**, 271A. See also, E. da Fano, *Asfalti*, 1934, **6**, 339; *Chem. Zentr.*, 1935, 1, 1806; *Brit. Chem. Abs.* **B**, 1935, 1124.

[208] See also J. Jachzel, *Asphalt Teer Strassenbautech.*, 1936, **36**, 101; *Chem. Abs.*, 1936, **30**, 5751; *J. Inst. Pet. Tech.*, 1936, **22**, 271A.

[209] H. Weber, *Proc. World Petroleum Congr.*, 1933, **2**, 669.

The following procedure[211] has been suggested for estimating the stability of emulsions: 1 g. is placed in a porcelain crucible (1 to 1¼ inch diameter) and concentrated by stirring under an air current at 18-20°C. This is continued until coagulation occurs, generally in ½ to ¾ hour. At this point the residual water content is determined by drying at 110°C. Characteristic values for different types of emulsions are:

Unstable Emulsions (fast)	15-25%	Residual Water
Semi-Stable Emulsions (medium)	8-10%	" "
Stable Emulsions (slow)	5-8%	" "

Another test (Sedimentation test) involves placing 500 cc. of the emulsion in a tall glass cylinder, covered to prevent evaporation, and after 5 days siphoning off the top 450 cc. The remaining 50 cc. plus sediment are then removed and loss on heating ascertained, the final heating period being 3 hours at 325°F. If during standing the sample in the cylinder exhibits creaming, i.e., the sediment floats instead of sinking to the bottom of the container, then the upper 50 cc. are withdrawn and loss on heating determined. The percentage of total solids thus found in the most concentrated layer withdrawn should not differ by more than 3 per cent from that in an equal volume of the initial asphalt emulsion.

One method[212] for measuring particle size comprises diluting 0.1 g. of the emulsion with 30 ml. of sodium oleate solution (1.5 to 2 per cent concentration), adding this to a standard haemacytometer cell, and taking a microphotograph. The number of particles are then counted per square (0.0025 sq. mm.) in the picture. Since the depth of the cell is 0.1 mm., the volume of solution per unit square is 0.00025 cu. mm. or 0.00025×10^{-3} cc. The mean radius (r) of the particles may then be calculated according to the formula

$$r = \sqrt[3]{\frac{3}{4\pi d} \times \frac{WB}{30} \times 0.00025 \times 10^{-3} \times \frac{n}{N}}$$

in which W is the weight of emulsion, B is the bitumen content and d its density, N is the total number of particles counted, and n the number of squares in which they appear.

Other inspections which are often made include total bitumen content, viscosity (usually Engler), resistance to low temperatures, homogeneity or screen test, i.e., proportion of asphalt held back when the emulsion is poured through a 20-mesh screen, water content, and stability to dilution with water.[213]

Methods outlined by the American Society for Testing Materials[214] for testing asphalt emulsions include measurement of viscosity, residue on distillation, percentage of water, miscibility with water, settling on standing, demulsibility, freezing test, residue on sieving, and coating test on stones. Percentage of water is determined by mixing the emulsion with an equal volume of a light oil or coal-tar naphtha (b.p. 120-250°C.) and distilling. Demulsibility is measured by adding to 100 g. of emulsion 35 cc. of 0.02*N* (for quick-setting type) or 50 cc. of 0.1*N* calcium chloride (for mixing type of emulsion) with continuous stirring and then weighing the precipitated asphalt which is caught on a No. 14 standard sieve.

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[210] C. L. McKesson, *Proc. World Petroleum Congr.*, 1933, **2**, 689; *Brit. Chem. Abs.* **B**, 1934, 661.

[211] L. Kirschbraun, *Proc. World Petroleum Congr.*, 1933, **2**, 682; *Brit. Chem. Abs.* **B**, 1934, 661.

[212] Tests on Bituminous Emulsions for Road Use, *Proc. World Petroleum Congr.*, 1933, **2**, 674.

[213] See, A. Riis, *Proc. World Petroleum Congr.*, 1933, **2**, 630. P. le Gavrian, *Proc. World Petroleum Congr.*, 1933, **2**, 630; *Brit. Chem. Abs.* **B**, 1934, 661. L. Meunier, *Proc. World Petroleum Congr.*, 1933, **2**, 654; *Brit. Chem. Abs.* **B**, 1934, 661. Ohse, *Proc. World Petroleum Congr.*, 1933, **2**, 660. A. Stellwaag, *Bitumen*, 1936, **6**, 1; *Chem. Abs.*, 1936, **30**, 5402. C. A. Downing, *Proc. Amer. Soc. Testing Materials*, No. 78, **1935**; *Chem. Abs.*, 1935, **29**, 5644; *Brit. Chem. Abs.* **B**, 1936, 482. H. Kleinert, *Asphalt und Teer*, 1935, **35**, 194; *J. Inst. Pet. Tech.*, 1935, **21**, 163A.

[214] A.S.T.M. Tentative Standards, **1935**, D244-35T, D397-34T to D401-34T.

Much the same types of tests are suggested by the British Standards Institution[215] with some exceptions. For example, in determining the percentage of water, the diluent employed has a narrower boiling range (125-160°C.) than that given above. Also, the rate of breaking of emulsions is measured by the "lability test," the assumption being made that the cause of breaking is the evaporation of water. A small portion of emulsion is placed in a porcelain crucible and stirred gently with a specially designed glass rod while a current of air at 18-20°C. is blown carefully over the surface. The time is recorded for coagulation to take place as determined by the collection of coagulum on the stirring rod.

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[215] B. S. I. Standard Specification 434, 1935.

Chapter 52

Reduction of Carbon Monoxide to Hydrocarbons. The Kogasin Synthesis and Synthetic Petroleum

Because of the wide variety of substances that may be produced by the catalytic hydrogenation of carbon monoxide, considerable interest has been manifested (especially abroad) in this type of synthesis. There are primarily two distinct types of operation, one of which leads to the formation of oxygenated compounds, and the other to hydrocarbons. Differentiation between the two processes is that the first requires high pressure treatment whereas the second is carried out at substantially atmospheric conditions.

Since about 1923, the high-pressure method has been exploited commercially in the production of methanol, or synthetic wood alcohol. In the same year, Fischer and Tropsch[1] found that by using a catalyst of iron and potassium carbonate a mixture of higher alcohols and other oxygenated substances (the so-called "Synthol") could be obtained from carbon monoxide and hydrogen by similar treatment. Normal alcohols up to nonanol ($C_9H_{19}OH$), fatty acids ranging from formic up to octanoic ($C_7H_{15}COOH$) and numerous aldehydes, ketones and esters, together with small quantities of hydrocarbons, were isolated from the reaction product. On the other hand, when low pressures are involved, methane is the resultant, as was shown by Sabatier and Senderens[2] in 1902. Later (1918), Orlov[3] synthesized ethylene by reducing carbon monoxide in the presence of coke impregnated with nickel and palladium. However, in 1926, Fischer and Tropsch[4] reported that with iron, nickel and cobalt catalysts and with treatment at atmospheric pressure it was possible to produce a mixture of the higher hydrocarbons (the so-called "Synthin" or "Kogasin"), similar to petroleum hydrocarbons.[5]

This chapter will be devoted expressly to a discussion of the second method of treatment, that involving the use of ordinary pressure, because of the relation of its products to those of the petroleum industry. Numerous preliminary investigations, conducted both in Germany and in Japan, had indicated that certain of the Synthin fractions may have possible application as motor or Diesel fuels, and that heavier-molecular weight portions could be cracked to furnish additional yields of gasoline. As a matter of fact, Fischer[6] states that by 1934 pilot plant and semi-works scale apparatus were developed to such an extent in Germany that it was decided to build a large commercial unit. Construction along this line was undertaken at that time, and Fischer believed that in a short while the carbon monoxide-hydrogen synthesis would become an important factor in fulfilling the fuel requirements of Germany by creating what may be termed a "synthetic petroleum" industry.

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[1] F. Fischer and H. Tropsch, *Brennstoff-Chem.*, 1923, **4**, 276; *J.S.C.I.*, 1923, **42**, 1009A; *Chem. Abs.*, 1924, **18**, 459. *Ber.*, 1923, **56**, 2428; *J.S.C.I.*, 1924, **43**, 152B.

[2] P. Sabatier and J. B. Senderens, *Compt. rend.*, 1902, **134**, 514; *Chem. Zentr.*, 1902, 1, 802; *J.C.S.*, 1902, **82** (1), 333.

[3] E. I. Orlov, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1588; *J.C.S.*, 1909, **96** (1), 77. *Ber.*, 1909, **42**, 893; *Chem. Abs.*, 1909, **3**, 1400.

[4] F. Fischer and H. Tropsch, *Brennstoff-Chem.*, 1926, **7**, 97; *Chem. Abs.*, 1926, **20**, 2065. *Ber.*, 1926, **59**, 830; *Brit. Chem. Abs.* **B**, 1926, 475; *Chem. Abs.*, 1926, **20**, 2814.

[5] See Carleton Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., Inc., New York, **1930** for a discussion of the hydrogenation of carbon monoxide to give methanol, methane, Synthol and Synthin. See also N. W. Krase, *Trans. Am. Inst. Chem. Eng.*, 1936, **32**, 493 for a review of these processes.

[6] F. Fischer, *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 782; *J. Inst. Pet. Tech.*, 1935, **21**, 453A; *Brit. Chem. Abs.* **B**, 1936, 51; *Chem. Abs.*, 1936, **30**, 3968.

Special names have been given to the fractions obtained in the Synthin treatment. The lower boiling hydrocarbons (containing 2 to 5 carbon atoms per molecule), which are gases at ordinary temperatures, are called "Gasol." The oily portion is referred to as "Kogasin" and consists of a mixture of straight- or slightly branched-chain saturated and unsaturated hydrocarbons. The part of the oil boiling in the gasoline range (30° to 200°C.) is known[7] as Kogasin I and the high-boiling residue (over 200°C.) as Kogasin II. Two types of solid paraffin waxes are formed, one (that separated from Kogasin by cooling) melting at about 40°C. and the other at about 96°C. The latter substance is termed synthetic "Ceresin" because of its similarity to naturally occurring wax of the same name.[7a] The expression "Synthin" is but little used at present, because of the fact that at one time it was applied to the mixture of hydrocarbons obtained by reduction of the oxygenated compounds produced in the Synthol treatment. The reaction is now commonly known as the Kogasin or Fischer-Tropsch synthesis, the first specifically pertaining to oils prepared from water gas[8] and the second a more or less general term.[9]

MECHANISM

Fischer and Tropsch[10] have proposed a mechanism for the synthesis of the higher hydrocarbons from carbon monoxide and hydrogen based on the formation of intermediate metallic carbides. Thus, in the presence of catalysts such as finely divided nickel, cobalt or iron, carbon monoxide is thought to be reduced to elemental carbon, which unites with the finely divided metals to form carbides. The latter apparently are not the ordinary low carbon content substances which are stable at high temperatures, but are quite rich in carbon, and are stable only at relatively low temperatures. They are reduced by hydrogen to form methylene radicals (CH_2), which in turn polymerize. Fischer and Tropsch are of the opinion that this theory explains the removal of carbon (from the carbides) as higher hydrocarbons rather than as methane. Fischer and Koch[11] have suggested the existence of methyl (CH_3) and methinyl (CH) radicals in addition to methylene, which might give rise to some of the substances noted in the reaction mixture.

Two distinct types of interaction have been observed by Fischer[12] using different catalysts. With nickel and cobalt, for instance, at 200°C. the mechanism may be represented as:

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[7] The term "Kogasin" is a contraction of the German: Kohle-Gas-Benzine.

[7a] See E. H. E. Graefe, *Ole, Fette, Wachse, Seife, Kosmetik*, **1936** (13), 1; *J. Inst. Pet. Tech.*, 1937, **23**, 78A; *Chem. Abs.*, 1937, **31**, 241.

[8] F. Fischer, *Brennstoff-Chem.*, 1935, 16, 1; *Brit. Chem. Abs.* **B**, 1935, 179; *Chem. Abs.*, 1935, **29**, 1959.

[9] Reviews of the Fischer-Tropsch process for the synthesis of motor fuels have been given by: F. Fischer, *Gas. J.*, 1936, **216**, 278; *Chem. Abs.*, 1937, **31**, 238. *Colliery Guardian*, 1936, **153**, 719; *Chem. Abs.*, 1937, **31**, 239. *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 120, 782; *J. Inst. Pet. Tech.*, 1935, **21**, 170A; 453A; *Chem. Abs.*, 1936, **30**, 3968; *Brit. Chem. Abs.* **B**, 1936, 51. *Brennstoff-Chem.*, 1935, **16**, 1; *Brit. Chem. Abs.* **B**, 1935, 179; *Chem. Abs.*, 1935, **29**, 1959. G. Hugel. *Ann. combustibles liquides*, 1936, 11, 719; *Chem. Abs.*, 1936, **30**, 8570; *Brit. Chem. Abs.* **B**, 1937, 108. *Mining and Met.*, 1936, 17, 439; *Chem. Abs.*, 1936, **30**, 8570. M. Friedwald, *Rev. pétrolifère*, 1935, **634**, 733; *Chem. Abs.*, 1935, **29**, 5626; *Chem. Zentr.*, 1935, **2**, 1290; *Brit. Chem. Abs.* **B**, 1936, 1076. O. Feldman. *S. African Mining Eng. J.*, 1935, **46** (1), 361; *Chem. Abs.*, 1935, **29**, 7055; *Brit. Chem. Abs.* **B**, 1936, 915. H. Koch, *Glückauf*, 1935, **71**, 85; *Chem. Abs.*, 1935, **29**, 6401. H. Pichler, *Z. Ver. deut. Ing.*, 1935, **79**, 883; *J. Inst. Pet. Tech.*, 1935, **21**, 377A. S. Tsutsumi, *Repts. Imp. Fuel Research Inst. Japan*, 1935, **31**, 1; *Chem. Abs.*, 1935, **29**, 7627; *J. Fuel Soc. Japan*, 1933, **12**, 137; *Brit. Chem. Abs.* **B**, 1934, 132; *Chem. Abs.*, 1934, **28**, 1515. F. Fischer, O. Roelen and N. Feisst, *Brennstoff-Chem.*, 1932, **13**, 461; *Chem. Abs.*, 1933, **27**, 2017; *Brit. Chem. Abs.* **B**, 1933, 136. F. Rosendahl, *Montan. Rundschau*, 1933, **25**, 1; *Petroleum Z.*, 1933, **29** (6), 1; *Chem. Abs.*, 1933, **27**, 1861. A. D. Petrov, *J. Applied Chem.* (*U.S.S.R.*), 1932 , **5**, 274; *Chem. Abs.*, 1932, **26**, 4932.

[10] F. Fischer and H. Tropsch, *Ber.*, 1926, **59**, 830; *Brit. Chem. Abs.* **B**, 1926, 475; *Chem. Abs.*, 1926, **20**, 2814. *Brennstoff-Chem.*, 1926, 7, 97; *Chem. Abs.*, 1926, **20**, 2065.

[11] F. Fischer and H. Koch, *Brennstoff-Chem.*, 1932, **13**, 428; *Brit. Chem. Abs.* **B**, 1933, 50; *Chem. Abs.*, 1933, **27**, 2017.

[12] F. Fischer, *loc. cit.*

$$CO + 2H_2 + Co_3C \longrightarrow Co_3C_2 + H_2O + H_2 \longrightarrow Co_3C + H_2O + (CH_2)$$

Under these conditions carbon monoxide is reduced to water and a higher metallic carbide (indicated by Co_3C_2). The latter is decomposed in a second step, giving rise to hydrocarbons by polymerization of the methylene radicals. On the other hand, iron behaves in quite a different manner. Fischer has suggested the following reaction with this catalyst at 250°C.:

$$2CO + H_2 + Fe_3C \longrightarrow Fe_3C_2 + CO_2 + H_2 \longrightarrow Fe_3C + CO_2 + (CH_2)$$

The difference between these two equations is that nickel and cobalt favor the union of 2 molecules of hydrogen and 1 of carbon monoxide, resulting in the formation of water, whereas with iron, 2 molecules of carbon monoxide and 1 of hydrogen unite and produce carbon dioxide as the by-product.[13]

THERMODYNAMIC CONSIDERATIONS

The application of thermodynamic principles to the Fischer-Tropsch process leads to several interesting conclusions.[14] Using the mechanism proposed by these investigators and the approximate linear free energy-temperature relation derived by Parks and Huffman[15] for carbon monoxide, water, methane, ethane, benzene, cyclohexane, *n*-hexane, *n*-hexene and *n*-octane, the following over-all equations may be obtained for reactions occurring in the gas phase with nickel or cobalt catalysts:

(1) $CO + 3H_2 = CH_4 + H_2O_{(g)}$; $\Delta F^\circ = -51{,}300 + 56.2T$
(2) $2CO + 5H_2 = C_2H_6 + 2H_2O_{(g)}$; $\Delta F^\circ = -90{,}400 + 117.4T$
(3) $6CO + 9H_2 = C_6H_{6(g)} + 6H_2O_{(g)}$; $\Delta F^\circ = -173{,}200 + 240.9T$
(4) $6CO + 12H_2 = \text{cyclo-}C_6H_{12(g)} + 6H_2O_{(g)}$; $\Delta F^\circ = -224{,}700 + 335.6T$
(5) $6CO + 12H_2 = n\text{-}C_6H_{12(g)} + 6H_2O_{(g)}$; $\Delta F^\circ = -211{,}400 + 316.3T$
(6) $6CO + 13H_2 = n\text{-}C_6H_{14(g)} + 6H_2O_{(g)}$; $\Delta F^\circ = -241{,}300 + 350.2T$
(7) $8CO + 17H_2 = n\text{-}C_8H_{18(g)} + 8H_2O_{(g)}$; $\Delta F^\circ = -317{,}500 + 466.6T$

These equations are represented graphically in Fig. 307, together with the temperature limits for the Kogasin (hydrocarbon) and for the Synthol (alcohol) syntheses (represented by the solid vertical lines) and the optimum temperatures (indicated by the dotted vertical lines) for the various catalysts in common use.

Considering first the Kogasin range, it will be seen that the production of hydrocarbons from carbon monoxide and hydrogen is favored thermodynamically, as is evidenced by the large negative values of the standard free energy change (ΔF°) for the over-all reactions. In the series methane, ethane, *n*-hexane and *n*-octane, ΔF° becomes more negative with the size of the molecule, so that the formation of higher members of the series might be expected to be quite feasible. From his thermodynamic calculations, Smith[15a] stated that at about 300°C. and atmospheric pressure, it should be possible to obtain any of the paraffin hydrocarbons by reduction of carbon monoxide in the presence of appropriate catalysts. The validity of this conclusion has since been confirmed by the isolation and identification of some of the reaction products,[16] which included practically all the members of the aliphatic series from ethane to hectopentacontane ($C_{150}H_{302}$).

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[13] See also M. Friedwald, *Rev. pétrolifère*, 1935, **634**, 733; *Chem. Abs.*, 1935, **29**, 1959; *Chem. Zentr.*, 1935, **2**, 1290; *Brit. Chem. Abs.* **B**, 1936, 1076. H. Koch, *Glückauf*, 1935, **71**, 85; *Chem. Abs.*, 1935, **29**, 6401.

[14] Thermodynamic considerations of the Synthin and Synthol processes have been given by D. F. Smith, *Ind. Eng. Chem.*, 1927, **19**, 801; *Chem. Abs.*, 1927, **21**, 2783; *Brit. Chem. Abs.* **B**, 1927, 593. E. Audibert, *Ann. combustibles liquides*, 1933, **8**, 757; *Chem. Zentr.*, 1934, **1**, 978; *Brit. Chem. Abs.* **B**, 1934, 1049; *Chem. Abs.*, 1934, **28**, 461. For discussions of the thermodynamics of the Synthol reactions, see P. K. Frolich and D. S. Cryder, *Ind. Eng. Chem.*, 1930, **22**, 1051; *Brit. Chem. Abs.* **B**, 1930, 1553; *Chem. Abs.*, 1930, **24**, 5717 and G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, **1932**. This topic has also been incorporated in Chapter 54.

[15] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, **1932**.

[15a] D. F. Smith, *Ind. Eng. Chem.*, 1927, **19**, 801; *Chem. Abs.*, 1927, **21**, 2783; *Brit. Chem. Abs.* **B**, 1927, 593.

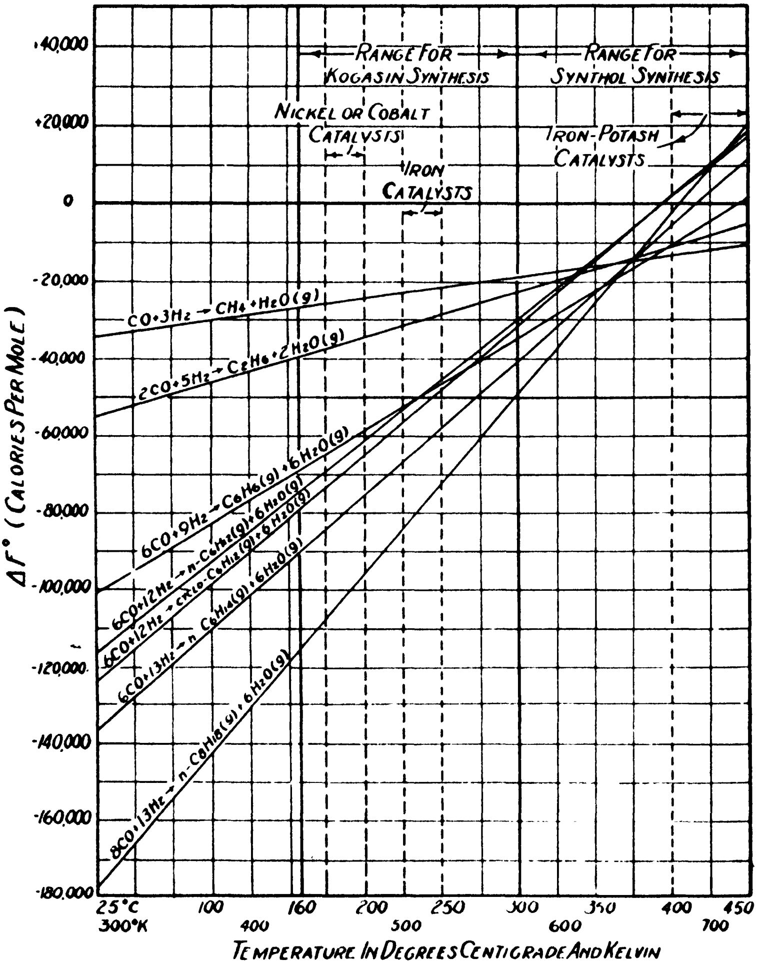

FIG. 307.—Molar Free Energy-Temperature Relationships in Reactions Yielding Hydrocarbons from Carbon Monoxide and Hydrogen.

Curves for the 4 six-carbon compounds, *n*-hexane, cyclohexane, *n*-hexene and benzene show that there is a slight thermodynamic favorability for the former rather than the cyclic, olefinic or other benzenoid types. The ΔF° for *n*-hexene is about 15,000 to 10,000 cal. less than that for *n*-hexane over this temperature range, so that the proportion of unsaturates in the reaction mixture may be predicted to be less than that of the corresponding saturated hydrocarbons. This is also in agreement with experimental observations, since the paraffinic type ordinarily predominate. (Nevertheless, the olefinic content may be increased by variations in the operating conditions, as will be discussed shortly.) From a thermodynamic viewpoint, cyclohexane and benzene (C_6H_6) might also be expected to be among the reaction products. However, as yet, reports as to the presence of the cyclic paraffin have only been negative, and the latter aromatic hydrocarbon is found only in traces.[17] Smith[18] believes that with the proper choice of a catalyst, the latter reaction could be made to go into effect.

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[16] See the section of this chapter devoted to the Chemical Composition of Products.

All of the free energy curves exhibit a decided positive slope, i.e., ΔF° assumes a more positive value (or the driving force of the reaction lessens) with increasing temperatures. At those employed in the Synthol reactions (about 300-450°C.) for the formation of oxygenated compounds, the free energy functions for all the higher hydrocarbons fall to relatively small negative or positive values. Ethane, and especially methane have smaller slopes than other hydrocarbons and consequently their formation is more highly favored than the higher members. At temperatures above 375°C., methane should be one of the principal resultants in the reduction. This, too, is borne out by experimental data.

The second mechanism proposed by Fischer[19] to account for the by-product carbon dioxide in the reaction mixture when iron catalysts are employed may be subjected to similar thermodynamic consideration. In this respect, the calculations of Smith[20] show that there is a somewhat greater tendency for the oxygen to form carbon dioxide rather than water. This means that there exists a greater driving force for the second type of reaction (that with iron contact agents). Consequently, it may be predicted that slightly higher temperatures can be used with iron catalysts, which is also in agreement with experimental facts.

THE INFLUENCE OF VARIOUS FACTORS IN THE KOGASIN SYNTHESIS

The influence of the numerous factors involved in the synthesis of hydrocarbons by the catalytic reduction of carbon monoxide has been summed up by Friedwald[21] as:

1. Increase of pressure → Synthol (methanol and higher alcohols and other oxygenated compounds
2. Increase in hydrogen content → methane
3. Decrease in hydrogen content → olefinic hydrocarbons
4. Increase of temperature → methane and finally carbon
5. Catalysts increase the degree of saturation of the product in the order iron, cobalt and nickel
6. Presence of carbon dioxide is without influence
7. Increase of life of catalyst gives an increase of light fraction and a decrease in oil content.

These points will be considered in due course in this chapter. It should be borne in mind, however, that the above-mentioned variations are only generalities and need further elaboration. But before so doing, it is advisable to discuss the catalysts and methods of their preparation.

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[17] H. Tropsch and H. Koch, *Brennstoff-Chem.*, 1929, **10**, 337; *Brit. Chem. Abs.* **B**, 1929, 1003; *Chem. Abs.*, 1930, **24**, 4919. S. Tsuneoka and K. Fujimura, *J. Soc. Chem. Ind., Japan*, 1934, **37**, Suppl. bind. 49; *Chem. Abs.*, 1934, **28**, 3570; *Brit. Chem. Abs.* **B**, 1934, 563.

[18] D. F. Smith, *loc. cit.*

[19] F. Fischer, *Brennstoff-Chem.*, 1935, **16**, 1; *Brit. Chem. Abs.* **B**, 1935, 179; *Chem. Abs.*, 1935, **29**, 1959. *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 782; *J. Inst. Pet. Tech.*, 1935, **21**, 453A; *Brit. Chem. Abs.* **B**, 1936, 51; *Chem. Abs.*, 1936, **30**, 3968.

[20] D. F. Smith, *loc. cit.*

[21] M. Friedwald, *Rev. pétrolifère*, 1935, **634**, 733; *Chem. Abs.*, 1935, **29**, 5626; *Chem. Zentr.*, 1935, **2**, 1290; *Brit. Chem. Abs.* **B**, 1936, 1076. Also F. Fischer, *Brennstoff-Chem.*, 1935, **16**, 1; *Brit. Chem. Abs.* **B**, 1935, 179; *Chem. Abs.*, 1935, **29**, 1959.

CATALYSTS

These play an extremely important part in the carbon monoxide-hydrogen synthesis and must have hydrogenating power even at very low temperatures. However, this latter property should not be too pronounced as saturation of methylene radicals occurs, thus giving rise to methane and inhibiting polymerization (of methylene) to higher homologues. Fischer and Tropsch[22] reported that the metals of the eighth group of the periodic table were applicable for the production of liquid hydrocarbons. Of these, finely divided cobalt was stated to be the best, with iron somewhat slower in its action, and nickel quite weak in its ability to form hydrocarbons other than methane. Fujimura and Tsuneoka[23] disagree with this observation and assert that in the range of 190 to 200°C., pure nickel gives better yields of liquid than cobalt. However, the contact agents in most general use are seldom the pure metallic elements themselves, as it has been observed that their effectiveness is greatly enhanced by the addition of various promoters. Furthermore, the manner of preparation also exerts an enormous influence not only on the yield of products but also on the life of the catalyst. Each of these factors will now be discussed briefly.[24]

Fischer and Tropsch[25] recommended mixing 1 to 3 parts of other substances, such as the oxides of chromium, zinc, beryllium and rare earth metals, and metals such as uranium, silicon, magnesium and manganese and activated carbon, to the above mentioned finely divided metals of the eighth group. According to Fujimura and Tsuneoka[26] the activity of nickel-thorium dioxide catalysts (containing 18 per cent ThO_2) is greatest at 195°C., and can be markedly increased by the addition of small amounts of potassium carbonate or rubidium carbonate. Nickel-manganese compositions are said to be adversely affected by sodium or potassium carbonate, but are improved by rubidium carbonate. Chromium and uranium may also be added. Subsequent investigations by these workers[27] using oxides of chromium, molybdenum, tungsten and uranium with nickel-manganese catalysts show that the promoting influence increases with the atomic weight of the metal. Of the numerous mixtures employed, the maximal results were obtained with thoria, alumina and fuller's earth as accelerators. Nickel-manganese-copper (15 per cent Mn and 0.5 per cent Cu) contact material was also reported to be an effective combination. The activity of mixtures of nickel and thoria, nickel and alumina and nickel and barium oxide (each containing 90 per cent Ni and 10 per cent promoter) and nickel-silica (80 per cent Ni, 20 per cent SiO_2) were studied by Muszkat.[28] His results indicate that, over periods of 50 hours usage, the first three pairs are practically unaffected, but the latter (Ni-SiO_2) lost 80 per cent of its catalytic ability during the operations. However, the presence of oxygen in the reaction mixture instantly inactivated all of these. Klyukvin and Vol'nov[29] noted that nickel-thorium, nickel-thorium-mercury and nickel-magnesium masses were satisfactory for the production of gasoline, giving optimum conversions of 100 g. per cubic meter of gas, or 30 to 40 per cent. On the other hand, Tsutsumi[30] reported a yield of 168 g. of total liquids from 1 cubic meter of gas using a nickel catalyst to which was added 20 per cent of manganese, 8 per cent of uranous-uranic oxide (U_3O_8) and 4 per cent of thorium oxide.

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[22] F. Fischer and H. Tropsch, *Ber.*, 1926, **59**, 830; *Chem. Abs.*, 1926, **20**, 2814; *Brit. Chem. Abs.* **B**, 1926, 475.

[23] K. Fujimura and S. Tsuneoka, *J. Soc. Chem. Ind., Japan*, 1933, **36**, Suppl. bind. 119; *Brit. Chem. Abs.* **B**, 1933, 452; *Chem. Abs.*, 1933, **27**, 3133.

[24] Although most of the catalytic reductions are conducted in the vapor phase, they may be carried out in the liquid phase, as by means of a finely divided solid catalyst suspended in oil. See F. Fischer and H. Küster, *Brennstoff-Chem.*, 1933, **14**, 3; *Chem. Abs.*, 1933, **27**, 2793; *Brit. Chem. Abs.* **B**, 1933, 211. Consult also M. Pier, German P. 630,824, 1936, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1937, **31**, 227.

[25] F. Fischer and H. Tropsch, *loc. cit.*

[26] K. Fujimura and S. Tsuneoka, *loc. cit.*

[27] K. Fujimura and S. Tsuneoka, *J. Soc. Chem. Ind., Japan*, 1933, **36**, Suppl. bind. 413; *Brit. Chem. Abs.* **B**, 1933, 773; *Chem. Abs.*, 1933, **27**, 4997.

[28] K. Muszkat, *Przemysl Chem.*, 1934, **18**, 483; *Chem. Abs.*, 1935, **29**, 6022; *Brit. Chem. Abs.* **B**, 1935, 132.

Fischer and Koch[31] obtained up to 153 cc. of liquid hydrocarbons per cubic meter of gas mixture, or 71 per cent of the theoretical, with catalysts of cobalt and 18 per cent thorium or 15 per cent manganese. These were imbedded on kieselguhr carriers. Fujimura[32] used a mixture of 8 parts of cobalt, 1 part of copper, 0.15 part of thorium, 0.15 part of uranium and 9.3 parts of starch, also carried on kieselguhr. Silver is said to be superior to copper as a promoter for cobalt, according to Tsutsumi.[33]

Gillet[34] investigated the relation between yield and catalyst and holds that iron with additions of nickel, manganese, aluminum, thorium or cobalt, either singly or together, is the most effective type of contact agent. In this connection it is of interest to note that Fischer and Meyer[35] reported that incorporation of iron with mixed nickel-cobalt catalysts decreases their activity. Ghosh and Sen[36] studied the effects of iron-copper combinations containing nickel, cerium and thorium. The maximum conversion to liquids that they obtained (43.4 per cent) was with a mixture composed of 4 parts of iron, 1 of copper, 0.25 of nickel, 0.0041 of cerium and 0.0296 of thorium. Braune[37] advocated the addition of small quantities of halides of alkaline earth metals to iron, as for instance, calcium chloride to magnetic iron oxide (Fe_3O_4). The inclusion of small quantities (0.005 mole) of sodium carbonate in equimolar mixtures of copper-iron catalysts is also said to increase the productivity of the mass.[38] Lefebvre and Le Clerc[38a] report that an iron oxide corresponding to magnetite causes mainly the formation of gasoline hydrocarbons from carbon monoxide and hydrogen. However, the presence of potassium (presumably as $KFeO_2$) in the catalyst caused heavy aliphatic hydrocarbons to be produced also.

Fujimura[39] has stated that the physical condition of the catalyst is just as important as its chemical composition. Both the manner of preparation and also the reaction temperature are of significance in determining the life of the contact mass.[40]

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[29] N. A. Klyukvin and Y. N. Vol'nov, *Khim. Tverdogo Topliva*, 1933, **4**, 355; *Chem. Abs.*, 1934, **28**, 6279; *J. Inst. Pet. Tech.*, 1935, **21**, 128A; *Brit. Chem. Abs.* **B**, 1935, 54.

[30] S. Tsutsumi, *Rept. Imp. Fuel Research Inst. Japan*, **31**; *J. Fuel Soc. Japan*, 1935, **14**, 110; *J. Inst. Pet. Tech.*, 1936, **22**, 23A; *Brit. Chem. Abs.* **B**, 1936, 7; *Chem. Abs.*, 1936, **30**, 845.

[31] F. Fischer and H. Koch, *Brennstoff-Chem.*, 1932, **13**, 61; *Brit. Chem. Abs.* **B**, 1932, 376; *Chem. Abs.*, 1932, **26**, 2582.

[32] K. Fujimura, *J. Soc. Chem. Ind., Japan*, 1932, **35**, 179 (Suppl. bind.); *Chem. Abs.*, 1932, **26**, 4444; *Brit. Chem. Abs.* **B**, 1932, 666. See also S. Watanabe, K. Morikawa and S. Igawa. *J. Soc. Chem. Ind., Japan*, 1934, **37**, Suppl. bind. 142; *Chem. Abs.*, 1934, **28**, 5648; *Brit. Chem. Abs.* **B**, 1934, 612.

[33] S. Tsutsumi, *loc. cit.*

[34] A. Gillet, ***Rev. universelle mines***, 1935, **11**, 180; *Chem. Abs.* 1935, **29**, 4561. See also S. Watanabe and K. Morika, *J. Soc. Chem. Ind., Japan*, 1933, **36**, 226 (Suppl. bind.); *Brit. Chem. Abs.* **B**, 1933, 738.

[35] F. Fischer and K. Meyer, *Ber.*, 1934, **67**, 253; *Chem. Abs.*, 1934, **28**, 2871; *Brit. Chem. Abs.* **A**, 1934, 389.

[36] J. C. Ghosh and S. Sen. *J. Indian Chem. Soc.*, 1935, **12**, 53; *Chem. Abs.*, 1935, **29**, 3903; *Brit. Chem. Abs.* **B**, 1935, 484.

[37] A. Braune, German P. 597,515, 1934, to Gewerkschaft Victor. Stickstoffwerke; *Chem. Abs.*, 1934, **28**, 5467.

[38] S. Kodama and K. Fujimura, *J. Soc. Chem. Ind., Japan*, 1931, **34**, Suppl. bind. 14; *Brit. Chem. Abs.* **A**, 1931, 439; *Chem. Abs.*, 1931, **25**, 1952. *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1936, **29**, 272; *Chem. Abs.*, 1936, **30**, 8570; *Brit. Chem. Abs.* **A**, 1936, 1212.

[38a] H. Lefebvre and G. Le Clerc, *Compt. rend.*, 1936, **203**, 1378; *Chem. Abs.*, 1937, **31**, 936.

[39] K. Fujimura, *J. Soc. Chem. Ind., Japan*, 1932, **35**, 179 (Suppl. bind.); *Brit. Chem. Abs.* **B**, 1932, 666; *Chem. Abs.*, 1932, **26**, 4444.

[40] I. B. Rapoport, A. P. Blyudov, L. Shevyakova and E. Frantzuz, *Khim. Tverdogo Topliva*, 1935, **6**, 221; *Chem. Abs.*, 1935, **29**, 7617; *J. Inst. Pet. Tech.*, 1936, **22**, 98A; *Brit. Chem. Abs.* **B**, 1937, 108.

Fischer[41] has compiled a list of 9 catalysts (See Table 227) together with their method of formation in order to show their relation to the yield of liquid products and the life of the catalyst (i.e., the time required for the catalyst to lose 80 per cent of its initial activity, as indicated by the conversion of the gases to liquids). In the case of cobalt-thorium-kieselguhr it will be noted that the precipitated contact mass gives a slightly higher yield of liquid products and has more than twice the life of an analogous material obtained by decomposition methods (such as by thermal treatment, as will be discussed shortly). Those compositions containing iron have a relatively short span of activity and also furnish relatively low yields of liquid, according to these data of Fischer. Tsutsumi[42] found that by using an excess of hydrogen over the ratio: $CO:H_2 = 1:2$, both the life of the contact mass and the quantity of gasoline may be increased.

TABLE 227.—*Yield of Liquid Products and Duration of Activity of Some Catalysts for the Carbon Monoxide-Hydrogen Synthesis from Water Gas.*

	Method of Preparation	Yield of Liquid g. per cubic meter of water gas	Duration of Time for 80% Loss of Initial Activity, days
Fe-Cu-Mn-silica gel –0.4% K_2CO_3..	decomposed	about 30-35	8
Fe-Cu-kieselguhr................	precipitated	" 28	8
Ni-Th-kieselguhr................	precipitated	" 100	30
Ni-Mn-Al-kieselguhr.............	precipitated	" 105	45
Co-Th-kieselguhr................	precipitated	110	60
Co-Th-kieselguhr................	decomposed	105	25
Co-Mn-kieselguhr................	precipitated	105	30
Co-Ni-Si........................	skeleton	85	12
Co-Th-Cu-kieselguhr.............	precipitated	105	60

Preparation of Catalysts. One of the most common procedures is that recommended by Fischer.[43] According to this method, kieselguhr is suspended in water and solutions of nickel nitrate and thorium nitrate are added. The metals are precipitated as hydroxides (with sodium hydroxide), the insoluble substances filtered, washed free from occluded salts and dried. The product must be activated by reduction, which is accomplished by heating in a stream of hydrogen at 350°C. Aicher, Myddleton and Walker[44] prefer to modify this treatment in the case of nickel-magnesium-aluminum-kieselguhr catalysts. The metal nitrates (in solution) are mixed with the kieselguhr, and then precipitated with potassium carbonate. The resulting magma is boiled for about 15 minutes, filtered by suction and washed with hot water. The filter cake is dried, crumbled and moistened with a solution of ethyl orthosilicate in toluene. The moist powder is then pressed into rods about ¼ inch in diameter, which are exposed to moist air for 2 days and subsequently broken into pellets of the desired size. After several more days exposure, the granules are ready for reduction. The latter step is accomplished in the catalytic chamber by passing in hydrogen at 450-480°C. for several hours.

As an example of thermally decomposed catalysts, the method of Fujimura and Tsuneoka[45] may be cited. These workers make a composition, consisting of 8 parts of cobalt, 1 of copper, 0.2 of thorium and 0.1 of uranium, by adding starch to a solution of the nitrates of these metals, evaporating to dryness and calcining. The starch serves a dual purpose in this instance, furnishing carbon to reduce the oxides to the corresponding metals and at the same time effecting a desirable porosity of the mass. This catalyst is said to give a yield of gasoline of 145 cc. per cubic meter of gaseous reactants at 210°C. with one passage. Irradiation of the contact mass with 50,000 volt X-rays had no marked influence on its activity.

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[41] F. Fischer, *Brennstoff-Chem.*, 1935, **16**, 1; *Chem. Abs.*, 1935, **29**, 1959; *Brit. Chem. Abs.* **B**, 1935, 179.

[42] S. Tsutsumi, *Rept. Imp. Fuel Research Inst. Japan*, **31**; *J. Fuel Soc. Japan*, 1935, **14**, 110; *J. Inst. Pet. Tech.*, 1936, **22**, 23A; *Brit. Chem. Abs.* **B**, 1936, 7; *Chem. Abs.*, 1936, **30**, 845.

[43] F. Fischer, German P. 571.898, 1933; *Chem. Abs.*, 1933, **27**, 4239.

[44] A. Aicher, W. W. Myddleton and J. Walker, *J.S.C.I.*, 1935, **54**, 313T; *Chem. Abs.*, 1935, **29**, 8289; *Brit. Chem. Abs.* **B**, 1935, 885.

[45] K. Fujimura and S. Tsuneoka, *J. Soc. Chem. Ind., Japan*, 1932, **35**, Suppl. bind. 415; *Chem Abs.*, 1933, **27**, 16; *Brit. Chem. Abs.* **B**, 1933, 7.

Antheaume[46] has suggested adding sodium hydroxide to an equimolar solution of iron and copper nitrates and leaching the precipitate with water until the washings are faintly alkaline ($p\text{H} = 7.4$). About 2 per cent of potassium carbonate is added and the mass granulated, dried and reduced with hydrogen at 250°C. Catalysts prepared by precipitation with ammonia in place of sodium hydroxide generally show poor activity, but can be improved somewhat in this respect by omitting the potassium carbonate. X-Ray studies revealed that these iron catalysts consist of two iron oxides, ferric (Fe_2O_3) and magnetic (Fe_3O_4), but not free iron. The magnetic oxide was thought to be present in the form of solid solution. According to Lefebvre and Le Clerc[46a] thermomagnetic analysis indicated magnetite in a catalyst prepared by precipitation of ferric hydroxide from ferric nitrate solution with ammonia or sodium hydroxide and subsequent reduction with hydrogen. Addition of 1 per cent of potassium carbonate in the initial stage of this procedure gave a catalyst which contained, according to thermomagnetic analysis, a solid solution of potassium ferrite ($KFeO_2$) in cubic ferric oxide (Fe_2O_3).

Antheaume[47] believed that copper performs 3 functions in contact mass: it activates the catalyst, permits low-temperature reduction of the metallic oxides and acts as a stabilizer. Fischer and Meyer[47a] tried to lower the reduction temperature (450°C.) of nickel-manganese-aluminum mass by the addition of copper, but were unsuccessful. They also noted that simultaneous precipitation of copper with the other metals lowered the reactivity of the product. However, when copper oxide or carbonate was added to the precipitated catalyst, it exerted a promoting effect.

Alloy Skeleton Catalyst. Fischer and Meyer[48] have pointed out that there are many disadvantages to the use of certain highly active precipitated catalysts. In the first place, many of the contact agents of this type are too voluminous, and thus occupy too much space. Furthermore the heat conductivity is so poor that there is great danger of local overheating with consequent increased formation of gases in place of liquid products. Grinding and the application of hydraulic pressure have been suggested as methods of reducing the volume-weight ratio of some contact materials.

However, the Raney[49] method has been found satisfactory for producing so-called "alloy-skeleton" catalysts, which Fischer and Meyer report to be quite effective, incorporating a large surface into a small volume and enhancing the heat conductivity. In this method, metallic nickel is alloyed with aluminum or silicon, and the latter elements subsequently removed by dissolving in sodium hydroxide. Thus, nickel and aluminum are fused in a high frequency electric furnace. After cooling, the alloy is broken into pieces about the size of a pea, and heated in boiling water under a reflux condenser. A slight excess of sodium hydroxide (25 per cent solution) over that theoretically required to combine with the aluminum is added gradually over a period of about 6 hours. The clear solution of sodium aluminate is poured off and the nickel is washed 6 times with hot water. Silicon cannot be removed as readily as aluminum, and even after 18 to 20 hours' heating about 5 to 10 per cent of silicon remains in the contact mass, according to these workers. The finished catalyst is kept under water to prevent oxidation. The resulting nickel skeleton is activated by treatment with hydrogen at 350°C. Subsequent impregnation of the skeleton with thorium nitrate is said to have a promoting effect. Cobalt and cobalt-nickel catalysts may be made in a similar manner. Fischer and Meyer obtained yields up to 130 cc. of liquid products per cubic meter of gas (23 per cent of carbon monoxide and 46 per cent hydrogen) and with a feed stock having a high-content of reactants (containing 31.7 per cent carbon monoxide and 65 per cent hydrogen), conversions as high as 161 cc. per cubic meter were secured. These results were confirmed by Tsuneoka and Murata.[50] These investigators advocate a somewhat longer period of heating (24 hours) to effect the removal of silicon from the alloy and also elimination of the last traces of sodium hydroxide remaining in the pores of the mass by extraction with ethyl alcohol.

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[46] J. Antheaume, *Ann. combustibles liquides,* 1935, **10**, 472; *J. Inst. Pet. Tech.*, 1935, **21**, 336A; *Chem. Abs.*, 1935, **29**, 6396.

[46a] H. Lefebvre and G. Le Clerc, *Compt. rend.*, 1936, **203**, 1378; *Chem. Abs.*, 1937, **31**, 936. See also, effect of these two types of catalyst, cited earlier in the chapter.

[47] J. Antheaume, *loc. cit.*

[47a] F. Fischer and K. Meyer, *Brennstoff-Chem.*, 1933, **14**, 64; *Brit. Chem. Abs.* **B**, 1933, 375; *Chem. Abs.*, 1933, **27**, 4034

[48] F. Fischer and K. Meyer, *Ber.*, 1934, **67**, 253; *Chem Abs.*, 1934, **28**; 2871; *Brit. Chem. Abs.* **A**, 1934, 389. *Brennstoff-Chem.*, 1934, **15**, 84, 107; *J. Inst. Pet. Tech.*, 1934, **20**, 307A, 365A

[49] M. Raney, U. S. P. 1,563,587, Dec. 1, 1925 and 1,628,190, May 10, 1927; *Brit. Chem. Abs.* **B**, 1926, 81; 1927, 606; *Chem Abs.*, 1926, **20**, 515; 1927, **21**, 2116.

According to Tsuneoka and Murata[51] pretreatment of nickel-cobalt-silicon alloy catalysts with hydrogen is unnecessary, as no increase in activity can be obtained by reduction at 220°C. At 350° to 450°C. such treatment is said to be detrimental, and at the latter temperature completely deactivates the catalyst. Oxidation of the mass before or after the reduction is likewise thought to be unfavorable. These investigators also noted that the activity of the alloy skeleton decreased greatly with increasing particle size, except with cobalt skeletons. In the latter, a marked decrease in such grain size gives a loss in activity.[52] Manganese acts as a poison to the nickel-cobalt-silicon alloys, checking hydrogenation and accelerating polymerization. From a study of the relation between the gas contraction and the temperature used in reducing the catalyst, Watanabe, Morikawa and Igawa[53] concluded that greater activity is associated with lower temperature values.

PRESSURE

The effect of pressure on the carbon monoxide-hydrogen interaction has been demonstrated by Fischer and Küster.[54] They used an electrically heated horizontal cylindrical rotating autoclave of 3 liters capacity and a catalyst (200 g.) of the cobalt-thorium-copper-cerium-kieselguhr type (9 parts of Co, 2 of Th, 1 of Cu and 0.25 of Ce) suspended in 1 liter of paraffin oil.[55] The feed gas (consisting approximately of 28 per cent of carbon monoxide and 59 per cent of hydrogen) was kept in intimate contact with the suspended catalyst by rotation of the autoclave (100 r.p.m.). Table 228 summarizes the results of tests made at 250°C. and 1, 10, 30 and 50 atmospheres pressure.

From these data it will be noted that hydrocarbon production decreases greatly as the pressure is increased. The quantity of gasoline reached a maximum (33.0 cc. per cubic meter of gas) at atmospheric pressure. However, at higher pressures, the proportions of lower boiling liquid hydrocarbons is much greater, although the

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[50] S. Tsuneoka and Y. Murata, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1935, **27**, 23; *Brit. Chem. Abs.* **B**, 1935, 581; *Chem. Abs.*, 1935, **29**, 4551.

[51] S. Tsuneoka and Y. Murata, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), 1935, **27**, 23; *Chem. Abs.*, 1935, **29**, 4551; *Brit. Chem. Abs.* **B**, 1935, 581.

[52] S. Tsuneoka and Y. Murata, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), 1936, **30**, 1; *Chem. Abs.*, 1936, **30**, 8570; *Brit. Chem. Abs.* **B**, 1936, 1028.

[53] S. Watanabe, K. Morikawa and S. Igawa, *J. Soc. Chem. Ind., Japan*, 1934, **37**, Suppl. bind. 385; *Brit. Chem. Abs.* **B**, 1934, 867; *Chem. Abs.*, 1934, **28**, 6982.

[54] F. Fischer and H. Küster, *Brennstoff-Chem.*, 1933, **14**, 3; *Chem. Abs.*, 1933, **27**, 2793; *Brit. Chem. Abs.* **B**, 1933, 211.

[55] The reason for carrying out the reaction in the liquid phase rather than in the gaseous phase was to prevent spots of local overheating on the catalyst.

TABLE 228.—*Effect of Pressure on CO-H_2 Reaction Using Co-Th-Cu-Ce Catalyst.*

Pressure, atm.	1		10		30		50	
Temperature, °C.	250		250		250		250	
Gas Velocity								
Feed, liters/hr.	20		35.8		34.3		40.8	
Exit, liters/hr.	17.8		20		20		20	
Liquid Products, cc./cubic meter								
Oil	146.5		40.0		14.6		19.8	
Water-soluble alcohols	—		1.8		8.8		2.5	
Gasoline	33.0		23.9		13.1		14.5	
Total	179.5		65.7		36.5		36.8	
Contraction in volume, %	10.7		43.3		44.0		49.7	
Gas analysis: %	Feed	Exit	Feed	Exit	Feed	Exit	Feed	Exit
CO_2	2.3	3.4	3.0	8.7	2.3	7.2	2.3	21.9
O_2	0.0	0.3	0.2	0.2	0.0	0.4	0.0	0.1
CO	28.2	27.1	29.1	20.4	28.2	20.1	28.2	1.8
H_2	59.1	57.1	58.3	40.0	59.1	42.2	59.1	27.7
CH_4	2.9	3.0	1.5	7.6	2.9	10.4	2.9	27.9
C_2H_6	0.0	0.7	0.0	8.6	0.0	5.9	0.0	5.3
N_2	7.5	8.4	7.9	14.1	7.5	13.4	7.5	14.9

amount of total liquids decreases greatly. With increase of pressure the Kogasin process shows a distinct trend, encroaching more and more into the region of Synthol formation, in that alcohols, acids and other oxygenated compounds result.

Thus, Fischer and Küster believe that by means of proper control of the pressure, both Kogasin and Synthol can be produced simultaneously with a cobalt catalyst. Their experimental work indicates that for the generation of hydrocarbons, the pressure should be about one atmosphere.

TEMPERATURE

Fischer and Küster[56] also studied the effect of temperature on the carbon-monoxide-hydrogen reaction using the catalyst and apparatus just previously described. By carrying out the reactions in the liquid phase (i.e., by suspending the catalyst in oil) it was possible to control and also measure the temperature of the reaction much more closely. Thus, when the catalytic reduction of carbon monoxide takes place in the gas phase, it is more than likely that "active spots" on the solid catalyst have a much higher temperature than the average value as indicated by a thermometer. However, in the oil phase, a more equal distribution of temperature results, and therefore these investigators used a slightly higher average reaction temperature to compensate for this effect. Table 229 summarizes their data, obtained in experiments at 30 atmospheres pressure and temperatures of 200°, 210°, 220° and 250°C.

The yield of total liquid product is quite low, and under the pressure employed, the percentage of alcohols formed is appreciable. However, at 250°C. it will be noted that the proportion of gasoline is the highest, being almost 50 per cent of the total liquids. Likewise considerable amounts of lower hydrocarbons, such as methane and ethane, become evident at this temperature.

Control of Temperature and Design of Catalyst Chambers. According to Fischer[57] the optimum temperature for both cobalt and nickel catalysts at atmospheric pressure is approximately 180° to 200°C., and for iron, 230° to 250°C.

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[56] F. Fischer and H. Küster, *Brennstoff-Chem.*, 1933, **14**, 3; *Chem. Abs.*, 1933, **27**, 2793; *Brit. Chem. Abs.* B, 1933, 211.

[57] F. Fischer, *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 120; *J. Inst. Pet. Tech.*, 1935, **21**, 170A.

TABLE 229.—*Effect of Temperature on CO-H_2 Reaction Using Co-Th-Cu-Ce Catalyst.*

Temperature, °C	200		210		220		250	
Pressure, atm	30		30		30		30	
Gas Velocity								
Feed, liters/hr	22.5		25.8		30.2		43.6	
Exit, liters/hr	20		20		20		20	
Liquid Product, cc./cubic meter								
Oil	7.7		11.9		8.6		4.4	
Water-soluble alcohols	5.0		9.3		10.4		6.6	
Gasoline	2.1		5.6		6.8		9.7	
Total	14.8		26.8		25.8		20.7	
Contraction in volume, %	11.2		22.7		33.6		54.0	
Gas analysis: %	Feed	Exit	Feed	Exit	Feed	Exit	Feed	Exit
CO_2	3.2	2.8	2.5	4.0	2.5	4.7	2.5	9.7
O_2	0.0	0.3	0.3	0.0	0.3	0.4	0.3	0.5
CO	28.4	28.5	28.3	26.5	28.3	25.3	28.3	16.4
H_2	57.0	55.1	57.3	50.7	57.3	46.5	57.3	27.5
CH_4	2.4	2.8	3.1	6.5	3.1	7.8	3.1	23.0
C_2H_6	0.3	0.7	0.0	1.3	0.0	2.5	0.0	4.2
N_2	8.7	9.8	8.5	11.0	8.5	12.8	8.5	18.5

However, due to the fact that a considerable quantity of heat is liberated (with complete conversion, amounting to about 20 per cent of the heat of combustion of the feed gas) unless some control is exercised, the reaction temperature would rise several hundred degrees. This would result in the formation of methane and lower gaseous hydrocarbons, and finally carbon, in place of the desired liquids. The difficulty has been overcome by employing specially designed catalyst chambers from which the heat may be rapidly conducted away, by means of oil circulation or radiation.[57a].

A type of apparatus used for semi-commercial operations employs a nickel-manganese-alumina catalyst packed into narrow rectangular metal units about 2x20 cm. in cross-section and 5 m. long.[58] The cases are immersed in a thermostat of circulating oil. With chambers of this design, the temperature control was automatic, and no great difficulty was said to be experienced in maintaining the reaction temperature between 190° and 210°C. Audibert[59] has discussed a similar unit used by Fischer for pilot-plant operation. Thin flat rectangular cases having a volume of about 70 liters are made by welding iron sheets 5x1.2 m. in dimensions to tubes of about 15 mm. diameter. About 21.3 kilograms of catalyst are packed into the frame, which is also surrounded by oil. Units of these dimensions treat about 6.8 cubic meters of gas per hour and cannot furnish more than 12 kilograms of liquid per day (7 to 8 grams per liter of catalyst volume).

Aicher, Myddleton and Walker[60] state that the most favorable yields of gasoline are obtained when the temperature is controlled to within ±5°C. The condition places a sharp limit upon the distance between the center of any catalyst layer and the conducting walls of the reaction chamber. These investigators advocate for laboratory-scale experiments, tubes of 15 mm. diameter, set into an aluminum frame. The latter should be provided with electrical resistance coils for the initial heating and also a jacket for circulation of a cooling medium to carry off the excess heat of reaction.

[57a] See also British P. 451,177, 1936, to Studien- und Verwertungs-G.m.b.H.; *Brit. Chem. Abs.* **B**, 1936, 964; *Chem. Abs.*, 1937, **31**, 294.

[58] F. Fischer, O. Roelen and W. Feisst, *Brennstoff-Chem.*, 1932, **13**, 461; *Chem. Abs.*, 1933, **27**, 2017; *Brit. Chem. Abs.* **B**, 1933, 136.

[59] E. Audibert, *Ann. combustibles liquides*, 1933, **8**, 757; *Brit. Chem. Abs.* **B**, 1934, 1049; *Chem Zentr.*, 1934, **1**, 978; *Chem. Abs.*, 1934, **28**, 461.

[60] A. Aicher, W. W. Myddleton and J. Walker, *J.S.C.I.*, 1935, **54**, 313T; *Chem. Abs.*, 1935, **29**, 8289; *Brit. Chem. Abs.* **B**, 1935, 885.

EFFECT OF VARIATIONS IN THE COMPOSITION OF THE FEED GAS

The theoretical composition of the feed gas should be 1 volume of carbon monoxide to 2 of hydrogen, which represents the stoichiometric quantities required for maximum yield of liquids. However, industrial gases always contain these components in varying proportions and admixed with others, e.g., nitrogen. The effect of such variations will be discussed in this section.

Tsuneoka and Fujimura[61] studied the influence of varying the composition of mixtures of pure carbon monoxide and hydrogen using a nickel-manganese-thoria-kieselguhr catalyst. They concluded that an excess of carbon monoxide has no deleterious effect on the yield of liquids, but that an excess of hydrogen favors the formation of methane. From observations with ratios of carbon monoxide to hydrogen of 1 :1, 1 :1.35, 1 :2 and 1 :3, these workers averred that the optimum composition should lie between 1 :2 and 1 :2.1 for the production of liquids. This is in accordance with the theoretical considerations, assuming the average hydrocarbon formed to be nonane:

$$9CO + 19H_2 \longrightarrow C_9H_{20} + 9H_2O$$

Watanabe, Morikawa and Igawa[62] also experimented with mixtures of gas in approximately the same range (1 :0.97 to 1 :2.96). They do not wholly agree with the conclusion of Tsuneoka and Fujimura regarding an excess of carbon monoxide, and report that when this component is present in concentrations greater than that called for theoretically, the generation of gaseous olefins and carbon dioxide and also liquid products is accelerated while that of the gaseous paraffins is reduced. It was also pointed out that dilution of the feed gas with nitrogen and carbon dioxide favored production of carbon dioxide and gaseous olefins, but this time at the expense of the liquid product. This was attributed to the lowering of the partial pressure of carbon monoxide.

However, Fujimura and Tsuneoka[63] report that only large quantities of diluents exert an appreciable effect on the yield of liquid hydrocarbons. Using a feed stock consisting of 32.8 per cent carbon monoxide, 65 per cent hydrogen and 2.2 per cent nitrogen and a nickel-manganese-thoria-kieselguhr contact agent, 117 cc. of gasoline per cubic meter of gas (corrected for volume of inert constituents) was obtained. The above stock then was diluted with either methane, carbon dioxide or nitrogen, in approximately 10, 20 and 40 per cent concentrations, and treated under the same conditions. The yields of liquid boiling in the motor fuel range (calculated on the basis of active gas passed) from these tests are incorporated in Table 230.

TABLE 230.—*Effect of Dilution of Gaseous Feed Stock on Yield of Gasoline. Feed Stock: 32.8% CO, 65% H_2, 2.2% N_2*

Diluent	Yield in cc./cubic meter active gas		
	10%	20%	40%
Nitrogen	115	112	95
Methane	120	106	85
Carbon dioxide	111	91	90

Fujimura and Tsuneoka concluded that addition of less than 20 per cent of inert gas did not seriously affect the reaction, but that 40 per cent lowered the conversion to boiling liquids. They also noted that the greater the dilution, the lighter and more volatile became the oil produced.[64]

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[61] S. Tsuneoka and K. Fujimura, *J. Soc. Chem. Ind., Japan*, 1934, **37**, Suppl. bind. 463; *J. Inst. Pet. Tech.*, 1934, **20**, 615A.

[62] S. Watanabe, K. Morikawa and S. Igawa, *J. Soc. Chem. Ind., Japan*, 1935, **38**, Suppl. bind. 328; *Chem. Abs.*, 1935, **29**, 6401; *Brit. Chem. Abs.* **B**, 1935, 887.

[63] K. Fujimura and S. Tsuneoka, *J. Soc. Chem. Ind., Japan*, 1933, **37**, Suppl. bind. 704; *Chem. Abs.*, 1935, **29**, 1230; *Brit. Chem. Abs.* **B**, 1935, 293; *J. Inst. Pet. Tech.*, 1935, **21**, 90A. *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1934, **25**, 127; *Brit. Chem. Abs.* **B**, 1935, 132; *Chem. Abs.*, 1935, **29**, 1230.

Rapoport, Blyudov, Shevyakova and Frantzuz[65] suggest addition of small proportions of ammonia to the reacting gas to increase the yield of gasoline. This is said to be particularly effective with catalysts precipitated on fuller's earth.

In general, the effect of sulphur is to deactivate the catalyst, and therefore this element should be removed in operations involving commercial gases. (This matter will be discussed subsequently in this chapter.) Yet special investigations as to the action of hydrogen sulphide or carbon disulphide on nickel catalysts, indicate that small quantities of either of the two sulphur compounds actually increased the activity of a nickel-manganese-alumina (15 per cent Mn, 3 per cent Al_2O_3) catalyst but had no effect on a nickel-manganese-thoria mass, (15 per cent Mn, 3 per cent ThO_2).[66] Large amounts poisoned both catalysts, the latter being more readily susceptible. To diminish the activity of the first-mentioned contact agent to 50 per cent of its original value required 54 mg. of hydrogen sulphide per gram of nickel, whereas this same reduction for the other mass was secured with only 16 to 28 mg. of hydrogen sulphide or approximately 50 mg. of carbon disulphide per gram of nickel. The poisoning power of the latter substance was determined to be directly proportional to its concentration. That of hydrogen sulphide, however, varied with the logarithm of its concentration. On the basis that the deleterious alteration is due to the development of nickel sulphide, these workers calculate that only 3.5 per cent of the total nickel in the contact mass is active in forming higher hydrocarbons.

TIME OF CONTACT

Unfortunately there is no manner in which the time of contact can be evaluated in the synthesis. This is due to the fact that the gas undergoes a large contraction in volume and at the same time loses considerable velocity in passing through the layers of catalyst. However, the influence of the feed-gas velocity has been studied by Fischer and Küster[67] using the oil-suspended cobalt-thorium-copper-cerium catalyst mentioned previously. Experiments were carried out under operating conditions of 250°C. and 10 or 30 atmospheres pressure with constant outlet velocity of 20 liters per hour. The results of these investigators are given in Table 231. The data indicate that under the pressures used, formation of hydrocarbons is favored by relatively fast input-gas velocities, whereas slower rates (or longer periods of contact) induce the production of alcohols. In the test conducted at 30 atmospheres pressure and feed-gas velocity of 40 liters per hour, the increase in the proportions of methane and carbon dioxide is worthy of note.

However, Watanabe, Morikawa and Igawa,[68] using a cobalt-copper-thoria composite at 197°C. and atmospheric pressure, found that the yields of gasoline and water per liter of gas ($CO:H_2=33.1:64.7$) decreased with increasing gas velocity. They concluded that the optimum rate for production of gasoline was 1.1 liters per

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[64] S. Tsuneoka and Y. Murata (*Sci. Papers Inst. Phys. Chem. Research, Tokyo*, 1935, **28**, 48; *Brit. Chem. Abs.* **B**, 1935, 1081; *Chem. Abs.*, 1936, **30**, 270) have shown that it is impossible to predict the yield of oil by the decrease in volume of the gas.

[65] I. B. Rapoport, A. P. Blyudov, L. Shevyakova and E. Frantzuz, *Khim. Tverdogo Topliva*, 1935, **6**, 221; *J. Inst. Pet. Tech.*, 1936, **22**, 98A; *Chem. Abs.*, 1935, **29**, 7617; *Brit. Chem. Abs.* **B**, 1937, 108.

[66] K. Fujimura, S. Tsuneoka and K. Kawamichi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1934, **24**, 93; *Chem. Abs.*, 1934, **28**, 4655; *Brit. Chem. Abs.* **B**, 1934, 662.

[67] F. Fischer and H. Küster, *Brennstoff-Chem.*, 1933, **14**, 3; *Brit. Chem. Abs.* **B**; 1933, 211; *Chem. Abs.*, 1933, **27**, 2793.

[68] S. Watanabe, K. Morikawa and S. Igawa, *J. Soc. Chem. Ind., Japan*, 1935, **38**, Suppl. bind. 70; *Brit. Chem. Abs.* **B**, 1935, 484; *Chem. Abs.*, 1935, **29**, 3495.

TABLE 231.—*Influence of Feed-Gas Velocity on CO-H_2 Reaction Using Co-Th-Cu-Ce Catalyst*

Feed-Gas Velocity, liters/hr.	40		34.3		35.8		28.8	
Temperature, °C.	250		250		250		250	
Pressure, atm.	30		30		10		10	
Exit-gas velocity, liters/hr.	20		20		20		20	
Liquid Products, cc./cubic meter								
Oil	20.0		14.6		40.0		36.9	
Water-soluble alcohols	1.1		8.8		1.8		3.5	
Gasoline	11.6		13.1		23.9		5.7	
Total	32.7		36.5		65.7		46.1	
Contraction in volume, %	50.9		44.0		43.3		25.8	
Gas analysis, volume %	Feed	Exit	Feed	Exit	Feed	Exit	Feed	Exit
CO_2	3.0	19.4	2.3	7.2	3.0	8.7	2.3	4.1
O_2	0.2	0.1	0.0	0.4	0.2	0.2	0.0	0.1
CO	29.1	5.1	28.2	20.4	29.1	20.4	28.2	26.3
H_2	58.3	23.7	59.1	42.2	58.3	40.0	59.1	51.8
CH_4	1.5	27.2	2.9	10.4	1.5	7.6	2.9	5.3
C_2H_6	0.0	8.5	0.0	5.9	0.0	8.6	0.0	2.2
N_2	7.9	16.3	7.5	13.4	7.9	14.1	7.5	10.1

hour per gram of cobalt. At higher speeds, the conversion drops off, which these workers attribute as possibly being due to the time required for diffusion of the gases through the layer of products surrounding the catalyst. That the reaction, as well as its extent, is influenced by increasing the gas velocity is shown by the correspondingly increased yield of gaseous olefins and also the density of the condensate. The rate of input feed recommended by Fischer, Roelen and Feisst[69] for the most economical yields of gasoline is 75.5 liters per hour per liter of catalyst space.

Aicher, Myddleton and Walker[70] have derived an expression for estimating a "time factor" (for contact materials packed in tubes) which is approximately proportional to the actual time of contact. This quantity was obtained by plotting the relation between the flow of gas (empirically corrected for the volume occupied by the oil and water vapor in the reaction vessel) and the depth of the catalyst, and integrating the reciprocal of these curves in accordance with the general equation:

$$t = f\int\frac{dL}{V_x}$$

where t = the time factor, or time required to traverse a length L of catalyst, dL = an infinitesimal length of catalyst, f = cross-sectional area of the catalyst tube and V_x = the volume of gas and vapor. The relation between the time factor and the yield of oil resulting from blue water gas at various temperatures, shown in Fig. 308 was obtained by Aicher, Myddleton and Walker. The distinct flattening of the curves at longer periods of contact and high concentrations of liquid is attributed to the adsorption of the products on the surface of the contact agent, thus exercising a retarding action. The curves also indicate that the initial few inches of the catalyst bed perform much more work than the succeeding layers. Thus, the excessive liberation of heat during the reaction is quite likely to develop a "hot spot" which must be guarded against.

EFFECT OF RECYCLING

Since the yield of total liquids is about 55 to 65 per cent of the theoretical, the exit gases contain appreciable quantities of unreacted carbon monoxide and hydrogen. Recycling, that is, passing the exit gas over fresh contact masses, was attempted to increase the yields. Thus, by limiting the extent of initial reaction (such as by using relatively low temperatures, insufficient hydrogen or low gas velocities), condensing the products and returning the remaining gases for further catalytic treatment, the total conversion is said to be increased.[71] However, some doubt as to the economic feasibility of this type of operation has been expressed.[72]

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[69] F. Fischer, O. Roelen and N. Feisst, *Brennstoff-Chem.*, 1932, **13**, 461; *Chem. Abs.*, 1933, **27**, 2017; *Brit. Chem. Abs.* **B**, 1933, 136.

[70] A. Aicher, W. W. Myddleton and J. Walker, *J.S.C.I.*, 1935, **54**, 313T; *Chem. Abs.*, 1935, **29**, 8289; *Brit. Chem. Abs.* **B**, 1935, 885.

Aicher, Myddleton and Walker[73] have summarized the arguments in favor of a two-stage treatment as follows: (1) There is an increased throughput (i.e., the whole of the contact material is working at higher efficiency and consequently less metal is required for a given output). (2) Increased yield of oil per unit volume of feed gas. (3) By use of different contact materials in the two or more steps, a grading or variation in the unsaturated content of the hydrocarbons may be brought about. (4) The adsorption effect, causing deposition of hard waxes on the catalyst, is retarded. (5) The formation of gaseous hydrocarbons is reduced. The chief disadvantage is that the gas must be cooled after the first stage (to permit removal of the lower-boiling liquid hydrocarbons by treatment with carbon) and the residual gas reheated for a second passage. The volume of the latter gases normally lies between 50 and 55 per cent of the original, but Aicher, Myddleton and Walker point out that there is sufficient heat liberated in the process and in the spent residual

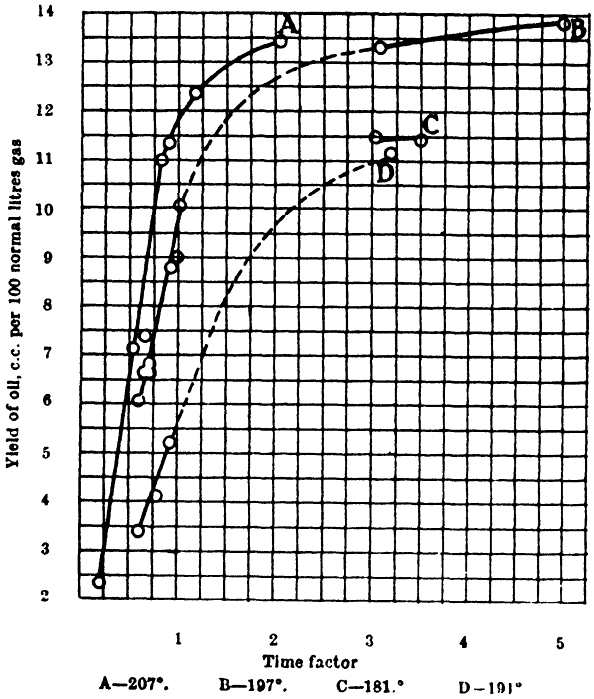

Fig. 308. Effect of Time Factor on Yield of Synthetic Oil from Blue Water Gas. (A. Aicher, W. W. Myddleton and J. Walker)

Courtesy Society of Chemical Industry

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[71] British P., 454,948, 1935, to Studien- und Verwertungsgesellschaft; *Brit. Chem. Abs.* **B**, 1936, 1191; *Chem. Abs.*, 1937, **31**, 1426. French P. 788,286, 1935; *Chem. Abs.*, 1936, **30**, 1383.

[72] M. Friedwald, *Rev. pétrolifère*, 1935, **634**, 733; *Chem. Abs.*, 1935, **29**, 5626; *Chem. Zentr.*, 1935, **2**, 1290; *Brit. Chem. Abs.* **B**, 1936, 1076.

[73] A. Aicher, W. W. Myddleton and J. Walker, *J.S.C.I.*, 1935, **54**, 313T; *Chem. Abs.*, 1935, **29**, 8289; *Brit. Chem. Abs.* **B**, 1935, 885.

gas to deal adequately and advantageously with the reheating required in the secondary stage.

These same workers[74] have investigated the yield of products obtained by one-, two- and three-stage treatments, using nickel-manganese-alumina-kieselguhr-silica masses. By plotting the results of these tests against the gas velocity, they obtained the curves shown in Fig. 309. Curve *A* refers to the single step treatment (25.5 cc. of catalyst), *B* is that for 2 stages, with the oil and water condensed after both stages and combined (50.9 cc. of catalyst space) and *C* is for 3 successive operations (79.0 cc. of catalyst space). The dotted lines in this figure connect points of corresponding flow for the different volumes of contact mass (or what amounts to the same, equal flow per unit volume of catalyst space) in each of the tests. Thus, considering only the one- and two-step experiments, at higher rates of flow it will be seen that the lines slope downward to the left, indicating that the one stage gave a higher yield than the two stages. However, at low rates of flow the 2-stage method shows a distinctly higher conversion than the former. According to these workers, 3-stage operations are not comparable with the others due to an unfavorable composition of the gas after it has passed through the two preceding treatments.

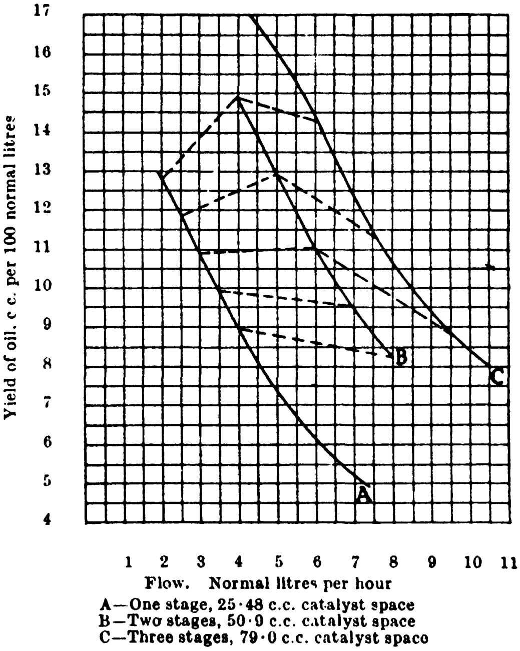

FIG. 309. Influence of Gas Velocity on Yield of Oil from Blue Water Gas in One-, Two- and Three-Stage Treatment. (A. Aicher, W. W. Myddleton and J. Walker)

Courtesy Society of Chemical Industry

Later research by Fischer and Pichler[75] proved definitely that by a step-wise treatment the overall output of liquid hydrocarbons could be increased by 10 to 20 per cent for the same weight of catalyst per volume of gas treated. They found it advantageous to arrange the rates of passage in successive stages to compensate for the gas contraction in such a manner that approximately the same volume of gas passes over the same quantity of catalyst. If the different steps are all carried out at the same temperature, a series of contact masses of successively diminishing activity should be employed. If, on the other hand, a uniformly active material is used, the temperature of the first stage should be somewhat lower than the others. Likewise, the life of the mass is extended somewhat better than in proportion to the number of steps. Fischer and Pichler report that with a 3-stage system a yield of 141 g. of liquid hydrocarbons has been obtained from 1 cubic meter of a gas containing 29.5 per cent carbon monoxide and 60 per cent hydrogen. This represents a 76 per cent conversion, based on the maximum theoretical yield of 185 g. per cubic meter.

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[74] A. Aicher, W. W. Myddleton and J. Walker, *loc. cit.*

[75] F. Fischer and H. Pichler, *Brennstoff-Chem.*, 1936, 17, 24; *Brit. Chem. Abs.* B, 1936, 306; *Chem. Abs.*, 1936, 30, 5764.

PRODUCTION OF METHANE AND OTHER GASEOUS HYDROCARBONS

As was mentioned earlier in this chapter, an increase in either the hydrogen content of the feed gas or in the reaction temperature favors the formation of methane in place of higher hydrocarbons. Certain catalysts, notably nickel, are particularly effective for promoting reduction.[76] Brückner and Jacobus[77] have investigated the addition of silica gel, alumina, thoria, and barium, strontium and calcium oxides to nickel for the reaction:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

at 300°C. The life of the contact mass is thought to be dependent largely upon the extent of formation of higher hydrocarbons, according to these workers. Therefore the inclusion of silica gel, which adsorbs these substances, prolongs the life of the contact material. Their results indicate that mixtures of 90 per cent nickel and 10 per cent alumina or thoria were the best, and that the activity of such mases could be promoted by the addition of alkaline earths, particularly barium oxide. On the other hand, cobalt decreases the effectiveness and copper completely inactivates the catalyst.

With nickel-alumina at 320°C. and a rate of flow of 200 liters per hour per liter of contact material, Karzhavina[78] obtained almost complete transformation of carbon monoxide into methane and carbon dioxide. Rapoport and Blyudov[79] reported a 99 per cent conversion at 270°C. with a nickel contact agent. With nickel-manganese combinations, however, reduction could be carried out at 200-204°C. These investigators noted that appreciable quantities of carbon dioxide resulted only at temperatures above 250°C. and that the simultaneous production of the latter substance and methane was promoted by a nickel-manganese-aluminum contact. Nickel carbonyl is said to exert a similar action, even at 150°C.[80] With molybdenum, no reduction of carbon monoxide occurs at 1 atmosphere pressure, according to Meyer and Horn.[81] At 100 atmospheres pressure, temperatures of about 400°C. are required to effect the formation of methane with molybdenum.

[76] In this respect, B. K. Klimov, V. A. Lanin and Z. T. Tikhonova, (*J. Chem. Ind.* (*Moscow*) **1934** (7), 50; *Chem. Abs.*, 1935, **29**, 321) suggested that the presence of methane in water gas prepared from peat coke is due to the catalytic reduction of the carbon monoxide by the coke.

[77] H. Brückner and G. Jacobus, *Brennstoff-Chem.*, 1933, **14**, 265; *Brit. Chem. Abs.* **B**, 1933, 772; *Chem. Abs.*, 1933, **27**, 5154. Nickel-cerium catalysts may also be used. See E. C. White (U. S. P., 1,908.202, May 9, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, **27**, 3684; *Brit. Chem. Abs.* **B**, 1934, 237) who uses this catalyst for estimating the amount of carbon monoxide in a gas mixture.

[78] N. A. Karzhavina, *J. Chem. Ind.* (*Moscow*), 1936, **13**, 598; *Brit. Chem. Abs.* **B**, 1936, 915; *Chem. Abs.*, 1936, **30**, 6533.

[79] I. B. Rapoport and A. P. Blyudov, *Khim. Tverdogo Topliva*, 1934, **5**, 625; *Chem. Abs.*, 1935, **29**, 2905; *Brit. Chem. Abs.* **B**, 1935, 1035.

[80] S. S. Urazovs'kii and N. A. Yakimkin, *Ukrain. Khem. Zhur.*, 1935, **10**, 44; *Brit. Chem. Abs.* **A**, 1935, 941; *Chem. Abs.*, 1936, **30**, 2476.

[81] K. Meyer and O. Horn, *Ges. Abhandl. Kenntnis Kohle*, 1934, 11, 389; *Chem. Zentr.*, 1934, **2**, 875; *Brit. Chem. Abs.* **B**, 1935, 390; *Chem. Abs.*, 1935, **29**, 6732.

Padovani[82] has discussed the application of the catalytic conversion of carbon monoxide to methane for the detoxification of gases. He states that at 10 atmospheres pressure and temperatures below 400°C., 85 to 90 per cent yields of methane can be obtained with a complex catalyst such as mixtures of nickel, iron, copper and silica gel.[83] Kemmer[84] proposes to retard the deposition of carbon, due to the reaction

$$2CO \longrightarrow CO_2 + C$$

by saturating the gas at 70°C. with water vapor and passing it over nickel masses at 300-380°C. In addition to the methane reaction, decomposition following the equation

$$CO + H_2O \longrightarrow H_2 + CO_2$$

is said to be effected. However, as Kemmer[85] has pointed out, reduction to methane requires a source of additional hydrogen, since three molecules are involved per molecule of carbon monoxide and would yield a gas of too high methane content. For this reason he suggests a two-step treatment, first interacting the gas with water, in accordance with the equation just given above, by which the carbon monoxide content may be reduced to 1 or 2 per cent. Then, by catalytic reduction, the remainder of the carbon monoxide may be converted into methane.

Perhaps the first evidence as to the possibility of forming higher hydrocarbons from carbon monoxide was that presented by Orlov.[86] He conducted a mixture of equal proportions of carbon monoxide and hydrogen over coke impregnated with metallic nickel and palladium at 95° to 100°C. The reaction product contained 6.6 per cent of ethylene but no methane or formaldehyde. Fischer and Pichler[87] have mentioned that with a silver contact agent or one of magnesite treated with hydrogen, considerable quantities of ethane are produced at high temperatures (600°C.) and pressures (over 70 atmospheres). It is interesting to note that Fuchs and Daur[88] obtained propene by passing a 2:1 mixture of methane and carbon monoxide over glowing pumice and that at 500-550°C. and 240 atmospheres, both propene and liquid hydrocarbons were secured.

PRODUCTION OF LIQUID HYDROCARBONS FROM CARBON DIOXIDE

In 1908, Orlov[89] pointed out that when carbon dioxide was substituted for carbon monoxide at 95° to 100°C. using a catalyst of coke impregnated with nickel, no hydrocarbons were formed. At a low red heat, however, both methane and ethylene were produced. He, therefore, concluded that the carbon dioxide was reduced to carbon monoxide by free carbon in the initial stages of the reaction. Subsequently, Fischer and Pichler,[90] from a study of the influence of carbon dioxide in the hydrogenation of carbon monoxide to liquids with nickel-magnesium-aluminum-kieselguhr combinations reported that interaction was not affected by the presence of the dioxide. Reduction of the higher oxide began only after all carbon monoxide had disappeared and resulted in the formation of methane. The latter observation was confirmed by Schuster, Panning and Bülow.[91]

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[82] C. Padovani, *J. usines Gaz*, 1934, **58**, 2; *Chaleur & ind.*, 1934, **15**, (167), 461; *Chimie et ind.*, 1934, **32**, 517; *Chem. Abs.*, 1934, **28**, 3872; *Brit. Chem. Abs.* **B**, 1934, 1044. See also F. Herglotz, *Z. öster. Ver. Gas- Wasserfach.*, 1932, **72**, 94; *Chem. Abs.*, 1932, **26**, 4159.

[83] See H. Cohn, British P. 352,864, 1929; and 366,563, 1929; *Chem. Abs.*, 1932, **26**, 3364; 1933, **27**, 2562; *Brit. Chem. Abs.* **B**, 1931, 959; 1932, 377.

[84] H. Kemmer, *Gas- u. Wasserfach*, 1932, **75**, 269; *Brit. Chem. Abs.* **B**, 1932, 448; *Chem. Abs.*, 1932, **26**, 3649.

[85] H. Kemmer, *Angew. Chem.*, 1936, **49**, 133; *Chem. Abs.*, 1936, **30**, 3204; *Brit. Chem. Abs.* **B**, 1936, 434.

[86] E. I. Orlov, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1588; *J.C.S.*, 1909, **96** (1), 77; *Ber.* 1909, **42**, 893; *Chem. Abs.*, 1909, **3**, 1400.

[87] F. Fischer and H. Pichler, *Ges. Abhandl. Kenntnis Kohle*, 1934, **11**, 386; *Chem. Zentr.*, 1934, **2**, 1062; *Chem. Abs.*, 1935, **29**, 6565; *Brit. Chem. Abs.* **B**, 1935, 390.

[88] W. Fuchs and R. Daur, *Ges. Abhandl. Kenntnis Kohle*, 1934, **11**, 327; *Chem. Zentr.*, 1934, **2**, 1062; *Brit. Chem. Abs.* **B**, 1935, 390; *Chem. Abs.*, 1935, **29**, 6566.

[89] E. I. Orlov, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1588; *J.C.S.*, 1909, **96** (1), 77; *Ber.* 1909, **42**, 893; *Chem. Abs.*, 1909, **3**, 1400.

[90] F. Fischer and H. Pichler, *Brennstoff-Chem.*, 1933, **14**, 306; *Brit. Chem. Abs.* **A**, 1933, 849; *Chem. Abs.*, 1933, **27**, 5937. See also H. Koch and H. Küster, *Brennstoff-Chem.*, 1933, **14**, 245; *Brit. Chem. Abs.* **B**, 1933, 737; *Chem. Abs.*, 1933, **27**, 5154.

Küster[92] reduced carbon dioxide to methane at temperatures of about 300°C. by means of a pure iron catalyst. Although the yields were small, the addition of copper, cobalt and nickel promoted reaction, and with cobalt contact masses, higher gaseous and liquid hydrocarbons resulted. A yield of 8.7 cc. of liquid per cubic meter of a $CO_2:3H_2$ mixture was obtained at 215°C. in the presence of a contact agent composed of 5 parts of iron, 5 of cobalt, 0.5 of copper and 1 per cent of potassium carbonate. However, using a ruthenium powder or ruthenium asbestos mass, Fischer, Bahr and Meusel[93] succeeded in reducing a mixture of carbon dioxide and hydrogen to methane at 100°C. By mixing 2 per cent of potassium carbonate with the ruthenium, both higher gaseous and liquid hydrocarbons were formed from carbon dioxide at 180° to 300°C.

Chemical Composition of the Products from Carbon Monoxide-Hydrogen Reaction

The chemical composition of the gaseous, liquid and solid substances obtained from carbon monoxide and hydrogen at atmospheric pressure is limited almost exclusively to two classes of hydrocarbons, paraffins and olefins. The exact proportions of these types can be varied over quite large ranges by the operating conditions. Thus, Fujimura and Tsuneoka[94] reported that although nickel favors the formation of saturates (up to 90 per cent of the total), cobalt on the other hand gives liquids possessing up to 57 per cent olefins. Furthermore, the proportion of gaseous hydrogen in the feed stock has a marked influence, high concentrations also tending towards the production of paraffins.[95]

Gases. Little information is available pertaining to the "Gasol" fraction (boiling below 30°C.). Fischer and Tropsch[96] and also Fischer and Koch[97] mention that this fraction consists of a mixture of hydrocarbons ranging from ethane to pentane. The olefinic content is given by Fischer[98] as 50 per cent by volume. Fujimura and Tsuneoka,[99] however, state that the composition of the exit gases varies greatly; with cobalt catalysts there was a small amount of carbon dioxide and some lower hydrocarbons, but with nickel the latter ranged from 6 to 35 per cent.

Liquids. Tropsch and Koch[100] examined the gasoline fraction obtained by the catalytic treatment of water gas and report that it consisted principally of olefins

[91] F. Schuster, G. Panning and H. Bülow, *Brennstoff-Chem.*, 1935, **16**, 368; *Chem. Abs.*, 1936, **30**, 3967; *Brit. Chem. Abs.* **B**, 1935, 1124.

[92] H. Küster, *Brennstoff-Chem.*, 1936, 17, 203; 221; *Brit. Chem. Abs.* **B**, 1936, 676, 727; *Chem. Abs.*, 1936, **30**, 7790; 1937, **31**, 1581.

[93] F. Fischer, T. Bahr and A. Meusel, *Ber.*, 1936, **69**, 183; *Brennstoff-Chem.*, 1935, **16**, 466; *Chem. Abs.*, 1936, **30**, 3401, 3967; *J. Inst. Pet. Tech.*, 1936, **22**, 44A; *Brit. Chem. Abs.* **B**, 1936, 180.

[94] K. Fujimura and S. Tsuneoka, *Sci. Papers Inst. Phys. Chem. Research*, (*Tokyo*), 1934, **24**, 79; *Chem. Abs.*, 1934, **28**, 4655; *Brit. Chem. Abs.* **B**, 1934, 662.

[95] S. Tsuneoka, *J. Soc. Chem. Ind., Japan*, 1933, **37**, Suppl. bind. 711; *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), 1934, **25**, 137; *Chem. Abs.*, 1935, **29**, 1231; *Brit. Chem. Abs.* **B**, 1935, 132.

[96] F. Fischer and H. Tropsch, *Ber.*, 1926, **59**, 923; *Chem. Abs.*, 1926, **20**, 2815; *Brit. Chem. Abs.* **B**, 1926, 475.

[97] F. Fischer and H. Koch, *Brennstoff-Chem.*, 1932, **13**, 428; *Brit. Chem. Abs.* **B**, 1933, 50; *Chem. Abs.*, 1933, **27**, 2017.

[98] F. Fischer, *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 782; *Brit. Chem. Abs.* **B**, 1936, 51; *Chem. Abs.*, 1936, **30**, 3968; *J. Inst. Pet. Tech.*, 1935, **21**, 453A.

[99] K. Fujimura and S. Tsuneoka, *loc. cit.*

[100] H. Tropsch and H. Koch, *Brennstoff-Chem.*, 1929, **10**, 337; *Brit. Chem. Abs.* **B**, 1929, 1003; *Chem. Abs.*, 1930, **24**, 4919.

(65 per cent) and paraffins. Only traces of aromatics (0.1 per cent of benzene and 0.4 to 0.5 per cent of toluene) and no naphthenes were found. By fractionation and the use of a modified mercuric acetate method,[101] whereby pure olefins were separated, the following hydrocarbons were isolated and identified: pentene-1, pentene-2, hexene-1, hexene-2, 3,3-dimethylpentene-1, heptene, octene-2, nonene, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, 3-methyloctane and *n*-nonane. Schaarschmidt and Marder[102] investigated the action of antimony pentachloride on the saturated hydrocarbons in the gasoline fraction and report that about 33 per cent of the paraffinic constituents consist of hydrocarbons containing a tertiary bound atom (such as isopentane and isohexane, for example), which are attacked by this reagent. Even the distillate corresponding in boiling point to *n*-heptane (obtained by repeated fractionation) contained some tertiary carbon atoms. The remainder of the hydrocarbons, which were unaffected by the antimony pentachloride, may have also possessed quaternary bound atoms, according to these workers. Fischer,[103] however, states that there is but little branching in the lower-boiling liquid paraffins.

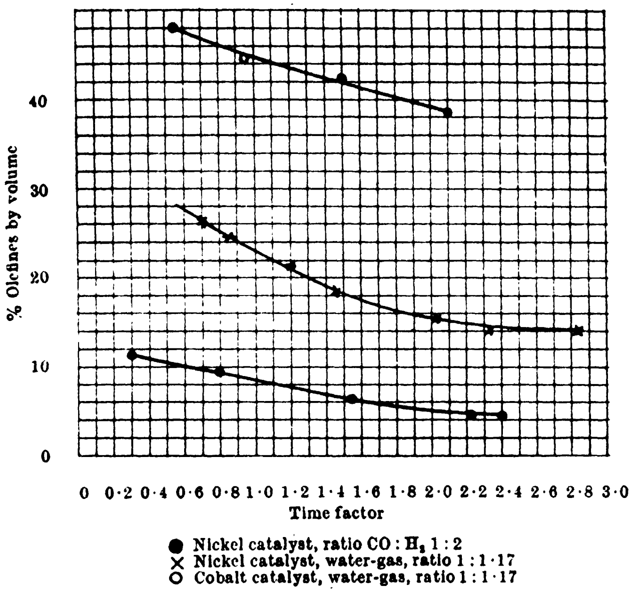

FIG. 310. Influence of Time Factor on Olefin Content of Synthetic Oil from Blue Water Gas. (W. W. Myddleton and J. Walker)

Courtesy Society of Chemical Industry

Tsuneoka and Fujimura[104] report the identification of normal paraffins ranging from pentane to undecane ($C_{11}H_{24}$) in the 30° to 200°C. portion of oil obtained with a nickel-manganese catalyst. The gasoline contained 92 per cent paraffins and 8 per cent olefins. Of the former, *n*-pentane, *n*-hexane, *n*-heptane and *n*-octane were the predominant components. These workers could not detect the presence of either aromatics or naphthenes.

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[101] See Chapter 50. Also Carleton Ellis, 'The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

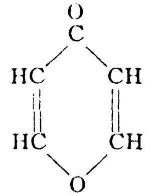
[102] A. Schaarschmidt and M. Marder, *Brennstoff-Chem.*, 1932, **13**, 412; *Brit. Chem. Abs.* **B**, 1933, 49; *Chem. Abs.*, 1933, **27**, 2017. See also, A. Schaarschmidt, *Petroleum Z.*, 1932, **28** (12), 1; *Brit. Chem. Abs.* **B**, 1932, 493; *Chem. Abs.*, 1932, **26**, 4706.

[103] F. Fischer, *Oel, Kohle, Erdoel, Teer*, 1935, 11, 120; *J. Inst. Pet. Tech.*, 1935, **21**, 170A.

[104] S. Tsuneoka and K. Fujimura, *J. Soc. Chem. Ind., Japan*, 1934, **37**, Suppl. bind. 49; *Brit. Chem. Abs.* **B**, 1934, 563; *Chem. Abs.*, 1934, **28**, 3570.

Myddleton and Walker[105] have studied the influence of the so-called "time factor" (mentioned previously in this chapter) on the percentage of olefins in the synthetic oil. Their results with nickel and cobalt catalysts are shown graphically in Fig 310. From this graph, it will be noted that higher proportions of unsaturates are formed with short periods of contact, cobalt rather than nickel contact masses and a deficiency in hydrogen. These investigators used the sulphuric acid-phosphoric acid method[106] for the determination of olefins, after they had established that no more than traces of aromatic hydrocarbons were present. Their work also confirmed the observation of Tsuneoka and Murata[107] that the percentage of unsaturated hydrocarbons decreases with boiling point of the fraction. Tsuneoka[108] has noted that there is a linear relation between the iodine number of the gasoline produced and the hydrogen content of the exit gas. It should be mentioned that Myddleton and Walker[109] found only monolefins in their product. This substantiates the previous observation of Tsuneoka and Murata[110] who had reported the complete absence of diolefins in the reaction mixture.[111]

Small amounts of oxygenated substances are produced even with operations carried out at atmospheric pressure, contrary to statements made by Fischer and Tropsch[112] in 1926. Thus, Tropsch and Koch[113] observed the presence of a substance, thought to be γ-pyrone:



which was separated from the 100-120°C. fraction of the lower-boiling oil. Tsuneoka and Fujimura[114] have investigated the aqueous solution formed in the reaction and report that it contains small quantities of alcohols, aldehydes, ketones and acids. In reference to the latter compounds, Koch, Pichler and Kölbel[115] noted that with cobalt catalysts a yield of 0.35 per cent of acids is produced by side reactions in the hydrocarbon syntheses. In the water layer of the reaction mixture, formic, acetic (about 2/3 of the total), propionic and butyric acids were identified. Unsaturated acids, however, were apparently completely absent. Higher fatty acids, containing 3, 5, 6, 7, 9 and 14 carbon atoms in the molecule were isolated from the oily portion, and amounted to 0.06 per cent by weight of the total Kogasin.

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[105] W. W. Myddleton and J. Walker, *J.S.C.I.*, 1936, **55**, 121T; *J. Inst. Pet. Tech.*, 1936, **22**, 356A; *Chem. Abs.*, 1936, **30**, 5393; *Brit. Chem. Abs.* **B**, 1936, 581.

[106] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[107] S. Tsuneoka and Y. Murata, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1935, **27**, 32; *Chem. Abs.*, 1935, **29**, 4551; *Brit. Chem. Abs.* **B**, 1935, 581.

[108] S. Tsuneoka, *J. Soc. Chem. Ind., Japan*, 1933, **25**, Suppl. bind. 711; *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1934, **25**, 137; *Brit. Chem. Abs.* **B**, 1935; 132; *Chem. Abs.*, 1935, **29**, 1231.

[109] W. W. Myddleton and J. Walker, *loc. cit.*

[110] S. Tsuneoka and Y. Murata, *loc. cit.*

[111] On the other hand, it has been stated (German P. 542,616, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, **26**, 3261) that the fraction boiling between 105° and 110° C. obtained by catalytic hydrogenation of carbon monoxide, is rich in terpenes, which can be removed by distilling over burnt lime.

[112] F. Fischer and H. Tropsch, *Ber.* 1926, **59**, 830; *Chem. Abs.*, 1926, **20**, 2814; *Brit. Chem. Abs.* **A**, 1926, 475.

[113] H. Tropsch and H. Koch, *Brennstoff-Chem.*, 1929, **10**, 337; *Brit. Chem. Abs.* **B**, 1929, 1003; *Chem. Abs.*, 1930, **24**, 4919.

[114] S. Tsuneoka and K. Fujimura, *J. Soc. Chem. Ind., Japan*, 1934, **37**, Suppl. bind. 49; *Chem. Abs.*, 1934, **28**, 3570; *Brit. Chem. Abs.* **B**, 1934, 563. K. Fujimura and S. Tsuneoka, *Sci. Papers Inst Phys. Chem. Research (Tokyo)*, 1934, **24**, 79; *Chem. Abs.*, 1934, **28**, 4655; *Brit. Chem. Abs.* **B**, 1934, 662.

[115] H. Koch, H. Pichler and H. Kölbel, *Brennstoff-Chem.*, 1935, **16**, 382; *Chem. Abs.*, 1936, **30**, 3970; *J. Inst. Pet. Tech.*, 1936, **22**, 45A; *Brit. Chem. Abs.* **B**, 1936, 6.

Koch and Ibing[116] have studied the higher boiling (220-350°C.) liquid Kogasin fraction. The oil was partially freed from paraffin wax by cooling to 0°C. and was then hydrogenated to saturate the olefins (4 to 7 per cent of the fraction). Upon repeated fractionation under reduced pressure, about 30 to 40 per cent of the original oil was resolved into *n*-paraffins ranging from decane ($C_{10}H_{22}$) to octadecane ($C_{18}H_{38}$). These were isolated and identified. The remainder consisted of isoparaffins with only slightly branched side chains.

Solids. According to Koch and Ibing[117] the solid paraffins cannot be concentrated with respect to their individual chemical purity by fractional distillation even at 10^{-5} mm. pressure. However, by an extraction method, using different solvents, a possible separation into groups of similar molecular weights and properties is indicated. Thus, the hard paraffin wax (so-called "Ceresin") removed from the catalysts on treatment with ether was resolved into soluble and insoluble constituents, in varying proportions, with minimum and maximum melting points of 40° and 106°C., respectively. The insoluble portion was next extracted with dichloroethylene, which gave products of melting points between 88° and 108°C. and insoluble residues. Upon extraction of the latter with chloroform for 200 hours, substances melting at 112° to 113° and 113° to 114°C. resulted. By renewed extraction with the latter solvent for 187 hours more, solids with melting points of 113-114.5°C. and 115.5 to 116.5°C. and molecular weights of 1750 and 2140, respectively, were isolated. From these experiments, Koch and Ibing concluded that the melting point increases similarly to the carbon-hydrogen ratio of the compounds, and that no homologs of the paraffin series have a higher melting point than about 118°C.

Koch and Ibing have pointed out also that the residues from the chloroform extraction represent the highest members of the saturated aliphatic hydrocarbons yet produced synthetically, and contain from 100 to 150 carbon atoms in the chain. When precipitated from hot benzene solution by alcohol, these appear as a white powder and after melting and solidifying, they are not scratched by the finger-nail. The specific gravity of the paraffin waxes is quite high, ranging from 0.938 for those melting at 40°C. to 0.965 for the largest molecular weight solids. These investigators concluded that the solid compounds are *n*-paraffins, with perhaps some isoparaffins, and have molecular formulas from $C_{20}H_{42}$ to about $C_{150}H_{302}$.

INDUSTRIAL APPLICATION OF THE FISCHER-TROPSCH SYNTHESIS OF HYDROCARBONS

Since about 1934, the rapid commercial development of motor fuel synthesis from carbon monoxide abroad has been phenomenal. It has been predicted that in 1937 half of the German requirements for automobile and aviation fuels will be produced synthetically.[118] This figure is said to be somewhat in excess of 2 billion gallons, or about one-seventh of the U. S. domestic consumption. When it is considered that the annual cracking capacity of German refineries in 1935 was only 121 million gallons,[119] some idea of the expansion along the lines of gasoline production becomes evident.

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[116] H. Koch and G. Ibing, *Brennstoff-Chem.*, 1935, **16**, 185; *Brit. Chem. Abs.* **B**, 1935, 709; *J. Inst. Pet. Tech.*, 1935, **21**, 300A; *Chem. Abs.*, 1936, **30**, 1984.

[117] H. Koch and G. Ibing, *Brennstoff-Chem.*, 1935, **16**, 141; *J. Inst. Pet. Tech.*, 1935, **21**, 406A; *Chem. Abs.*, 1935, **29**, 5642; *Brit. Chem. Abs.* **B**, 1935, 582.

[118] See *Chem. Industries*, 1936, **39**, 574.

[119] See Chapter 3.

In general, the Fischer-Tropsch process[120] may be summed up in four essential steps: (1) the preparation of the crude feed mixture, (2) partial desulphurization of the gas to free it of hydrogen sulphide, (3) further desulphurization to reduce the organic sulphur content within prescribed limits and (4) the catalytic treatment. A typical flow diagram for these operations is given in Fig. 311. The individual operations will be considered more in detail subsequently in this section. From Fig. 311 it will be seen that the fundamental procedure is as follows: the feed gas mixture is made in a gas producer of the conventional type by alternately introducing air and steam in a bed of incandescent coke. The gases are washed with water and filtered to remove coal dust and other entrained solid matter, and passed into a primary desulphuretting unit, where hydrogen sulphide is removed. Next the gas is fed into a secondary desulphurizing unit in which organically combined sulphur is eliminated. The sulphur-free gas is now introduced into the catalytic chambers. Here the temperature is maintained between very narrow limits by means of circulating oil. (The temperature used in this stage is dependent upon the nature of the catalyst and other conditions). The hot oil is used for generating steam in a small heat exchanger. The gas and liquid products leaving the contact apparatus are cooled and passed into a separator, where the oil and water are removed. The overhead from the separator is fed into a tower packed with activated carbon (water washing may be used in place of adsorption) to separate the lighter gasoline fractions from the exit gases.

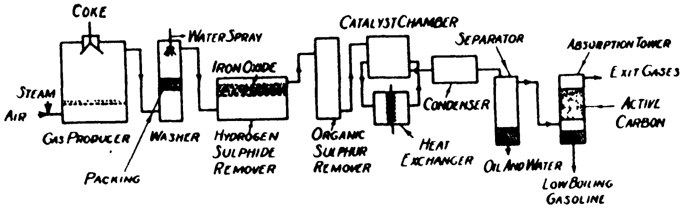

FIG. 311.—Flow Diagram of Fischer-Tropsch Synthesis.

PRODUCTION OF GAS MIXTURE

One of the basic requirements for the commercialization of this process is the availability of enormous quantities of carbon monoxide and hydrogen. These gases may be obtained from many sources as for instance, industrial gases, natural gas or coke. Fischer, Pichler and Reder[121] have discussed this topic and state that the gas mixture may be produced by mixing coke-oven gas with generator gas or with water gas, by direct gasification of coal, or by the interaction of methane, or higher hydrocarbons with steam or carbon dioxide[122] or with oxygen (partial oxidation).

[120] Reviews on the commercial Fischer-Tropsch process have been given by: F. Fischer, *Oel, Kohle, Erdoel, Teer,* 1935, 11, 120; 785; *J. Inst. Pet. Tech.*, 1935, **21**, 170A, 453A; *Chem. Abs.*, 1936, **30**, 3968; *Brit. Chem. Abs.* **B**, 1936, 51; *Brennstoff-Chem.*, 1935, **16**, 1; *Chem. Abs.*, 1935, **29**, 1959; *Brit. Chem. Abs.* **B**, 1935, 179. O. Feldman, *S. African Mining Eng. J.*, 1935, **46** (1), 361; *Brit. Chem. Abs.* **B**, 1936, 915; *Chem. Abs.*, 1935, **29**, 7055. M. Friedwald, *Rev. pétrolifère*, 1935, **634**, 733; *Chem. Abs.*, 1935, **29**, 5626; *Chem. Zentr.*, 1935, 2, 1290; *Brit. Chem. Abs.* **B**, 1936, 1076.

[121] F. Fischer, H. Pichler and R. Reder, *Brennstoff-Chem.*, 1932, **13**, 421; *Brit. Chem. Abs.* **B**, 1933, 49; *Chem. Abs.*, 1933, **27**, 2017. See also N. W. Krase, *Trans. Am. Inst. Chem. Eng.*, 1936, **32**, 493.

[122] See Chapter 10. Also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

One convenient method of producing these gases is by the well known water gas reaction, by the action of steam on coke at temperatures of about 1000°C.[123] according to the equation:

$$C + H_2O \longrightarrow CO + H_2$$

The resulting mixture thus should contain equal volumes of carbon monoxide and hydrogen, but according to Fischer[124] a 1:2 ratio of these gases (which has been found to be optimum) can be obtained by gasifying at low temperatures in the presence of a larger quantity of steam, in accordance with the equation:

$$H_2O + CO \longrightarrow H_2 + CO_2$$

The hydrogen deficiency in water gas can be made up in a number of other ways. For instance, Fischer, Pichler and Reder[125] reported that in the presence of a nickel catalyst, methane will react with steam at 800°C. and 1 atmosphere or 600°C. and 0.1 atmosphere pressure (at times of contact of less than 1 second) to give carbon monoxide.

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

Thus, by combining the water-gas reaction with the latter, a mixture of carbon monoxide and hydrogen in the proportion 1:2 can be formed. Likewise, the thermal decomposition of methane

$$CH_4 \longrightarrow C + 2H_2$$

may be utilized to augment the hydrogen content of the water gas.[126] Deficiencies in carbon monoxide may be made up by secondary reactions involving the reduction of carbon dioxide.[127] The latter may be accomplished in a variety of ways, as with coke,

$$CO_2 + C \longrightarrow 2CO$$

or with copper.[128] The possibility of using electrolytic hydrogen and carbon dioxide from gas wells has also been considered by Fischer.[129] From this discussion it will be seen that quite a wide variety of reactions are applicable for production of the feed stock gases.

Fischer, Pichler and Reder[130] suggested forming the gas mixture by passing coke-oven gas and steam over incandescent coke. In these experiments, a small water-gas generator was used, and the fuel bed alternately blown with air for 1 minute and then subjected to the action of the mixed steam and coke-oven gas for 3 minutes. The resulting gas had the composition: 2.4 per cent carbon dioxide, 0.4 per cent oxygen, 28.2 per cent carbon monoxide, 52.3 per cent hydrogen, 2.5 per cent methane and 14.2 per cent nitrogen. This mixture was reported to give a yield of 26.4 per cent gasoline based on the quantity of coal used. Subsequent work by

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[123] W. M. Cross (U. S. P. 1,860,138, May 24, 1932; *Brit. Chem. Abs.* **B**, 1933, 455; *Chem. Abs.*, 1932, **26**, 3906) has suggested the use of steam superheated to temperatures as high as 1500°C. for producing water gas.

[124] F. Fischer, *Oel, Kohle, Erdoel, Teer*, 1935, 11, 120; *J. Inst. Pet. Tech.*, 1935, **21**, 170A.

[125] F. Fischer, H. Pichler and R. Reder, *loc. cit.* See also R. Fussteig, *Chimie & industrie*, 1935, **34**, 3; *Brit. Chem. Abs.* **B**, 1935, 836; *Chem. Abs.*, 1935, **29**, 7058.

[126] See Chapter 7. Also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, **1934**.

[127] See M. Friedwald, *Rev. pétrolifère*, 1935, **634**, 733; *Chem. Abs.*, 1935, **29**, 5626; *Chem. Zentr.*, 1935, **2**, 1290; *Brit. Chem. Abs.*, **B**, 1936, 1076.

[128] The carbon dioxide may be obtained by decomposition of carbonates or bicarbonates. For examples, see J. J. Puig and R. Sunen-Beneded, French P. 784,742, 1935; *Chem. Abs.*, 1936, **30**, 484.

[129] F. Fischer, *Oel, Kohle, Erdoel, Teer*, 1935, 11, 782; *J. Inst. Pet. Tech.*, 1935, **21**, 453A; *Chem. Abs.*, 1936, **30**, 3968; *Brit. Chem. Abs.* **B**, 1936, 51.

[130] F. Fischer, H. Pichler and R. Reder, *Brennstoff-Chem.*, 1932, **13**, 421; *Brit. Chem. Abs.* **B**, 1933, 49; *Chem. Abs.*, 1933, **27**, 2017.

Fischer, Pichler and Kölbel[131] with a gas producer of 100 cubic meters per hour output showed that the ratio of carbon monoxide to hydrogen could be raised to 1 :2. This was accomplished by increasing the gasifying time to 4 minutes instead of the 3 minutes used in the earlier tests. The carbon dioxide content was reduced to 0.6 per cent and that of methane to 0.4 per cent. However, with a 1 minute blast and a 6 minute gasification period, the latter figures increased to 0.9 and 1.1 per cent respectively.

The theoretical yield of oil naturally depends upon the composition of the gas, the highest theoretically possible being given by a gas containing 33.3 per cent carbon monoxide and 66.6 per cent hydrogen. However, Fischer and Meyer[132] have used coke-oven gas, with a carbon monoxide content of only 5 to 6 per cent and obtained 22 cc. of total liquids (75 per cent of which boiled in the gasoline range) per liter of feed gas, using a nickel-manganese-aluminum catalyst. Aicher, Myddleton and Walker[133] have prepared a list of the common industrial gases together with the per cent of carbon monoxide available (i.e., with the necessary hydrogen for a 1 :2 ratio) and the theoretical yield of oil in gallons per 1000 cubic feet of gas, as is given in Table 232. According to these investigators, commercial yields of liquid hydrocarbons cannot be attained from gases containing less than about 24 per cent of carbon monoxide and 48 per cent of hydrogen.

TABLE 232.—*Theoretical Yields of Oil Obtainable from Industrial Gases in the Carbon Monoxide-Hydrogen Synthesis.*

	CO, Vol.% Available with Necessary H_2	Theoretical Yield of Oil in Gallons/1000 cu.ft. of Gas
Coke-oven gas	5.5	0.31
Cracked gas (coke-oven gas treated with steam at 900°C.)	19.2	1.09
Water gas	24.0	1.36
Water gas and coke-oven gas	25.3	1.43
Special water gas made at a lower average temperature	29.0	1.64
Cracked coke-oven gas and water gas	30.4	1.72

Sulphur Removal. All commercial gases contain sulphur, either as hydrogen sulphide or as mercaptans or in other chemical combinations, which exert a serious deactivation effect on the catalyst. According to Fischer,[134] the total sulphur content must be reduced to less than 0.2 g. per 100 cubic meters (approximately 0.1 grain per 100 cubic feet). This is usually done in two stages, (as indicated in the flow diagram, Fig. 311), the first for the removal of hydrogen sulphide and the second for organically combined sulphur. Desulphuretting is accomplished by passing the gas over layers of iron oxide. Details on the removal of the organic sulphur (second stage) in the commercial process are not available at present, however Aicher, Myddleton and Walker[135] have described a catalytic method which they used on a semi-commercial scale. The mercaptans and other sulphur-containing compounds are reduced to hydrogen sulphide by hydrogenation over a catalyst. The latter is prepared by mixing equal parts of copper oxide and lead chromate, adding a solution of ethyl orthosilicate in toluene, and pressing the paste into rods ¼ inch in diameter which are broken into convenient lengths. After several days exposure to moist air, to cause hydrolysis of the silicate ester and thereby obtain the desulphiding catalyst on a durable but porous support of silica, the mass is charged into iron tubes (about 2 or 3 inches in diameter) and reduced by passing the gas mixture through at a temperature of 370-400°C. for several hours. Hydrogen sulphide resulting from this treatment is removed by again passing the gas over a bed of iron oxide. In this manner it was possible to reduce the sulphur content of some gases from 30 grains per 100 cubic feet to approximately 1.1 grains per 100 cubic feet. The latter figure is still much too high, and therefore the gas was subjected to a second catalytic treatment. Instead of removing the hydrogen sulphide resulting from this operation with iron oxide, an alkaline solution of potassium ferricyanide was used. By this procedure, the sulphur content was lowered to about 0.1 grain per 100 cubic feet. According to these workers, the catalyst proposed showed no loss in activity during several months of continuous operation. The potassium ferricyanide solution, however, required continuous electrolytic oxidation to maintain it at working strength. Treatment at 150-300°C. with a catalytic mixture of 5 to 10 per cent of an alkali carbonate with oxides or hydroxides of iron has also been suggested for the removal of organic sulphur compounds.[136]

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[131] F. Fischer, H. Pichler and H. Kölbel, *Brennstoff-Chem.*, 1935, **16**, 401; *Brit. Chem. Abs.* **B**, 1936, 51; *Chem. Abs.*, 1936, **30**, 3970.

[132] F. Fischer and K. Meyer, *Ges. Abhandl. Kenntnis Kohle*, 1934, **11**, 497; *Chem. Zentr.*, 1934, **2**, 1061; *Chem. Abs.*, 1935, **29**, 6747; *Brit. Chem. Abs.* **B**, 1935, 390.

[133] A. Aicher, W. W. Myddleton and J. Walker, *J.S.C.I.*, 1935, **54**, 313T; *Chem. Abs.*, 1935, **29**, 8289; *Brit. Chem. Abs.* **B**, 1935, 885.

[134] F. Fischer, *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 120; *J. Inst. Pet. Tech.*, 1935, **21**, 170A.

[135] A. Aicher, W. W. Myddleton and J. Walker, *J.S.C.I.*, 1935, **54**, 313T; *Chem. Abs.*, 1935, **29**, 8289; *Brit. Chem. Abs.* **B**, 1935, 885.

CONTACT AGENTS

The catalysts recommended by Fischer[137] for commercial operations are of the cobalt type. Cobalt-thorium-kieselguhr (18 per cent Th), made by precipitation of the nitrates with sodium carbonate, are said to be among the best. (Similar masses formed by thermally decomposing the nitrates may also be used, but have a much shorter active life.) The cobalt-thorium-copper-kieselguhr catalysts (2 per cent of copper) are also employed since they can be reduced at very low temperatures. With contact materials of these types, yields of 100-130 grams of liquid hydrocarbons are obtained per cubic meter of the special water gas mentioned previously. Conversion is about 56 to 72 per cent of the theoretical (180 grams). Fischer states that the yield will undoubtably be greatly increased in the future after sufficient experience has been accumulated. He is also of the opinion that iron may eventually replace cobalt for large scale operation. Silica gel or asbestos may be substituted for kieselguhr in the contact masses, according to Friedwald.[138] Notwithstanding careful purification of the gas to lower its sulphur content to 0.2 g. per 100 cubic meters, poisoning of the catalyst cannot be avoided in runs of long duration. Fischer and Meyer[139] have proposed to compensate for this deactivation with nickel catalysts (which completely absorb the sulphur in the gases) by increasing the reaction temperatures slowly, about 25°C. over a period of 4 weeks. After this time has elapsed, however, a complete reconditioning of the catalyst is necessary. Fischer and Koch[140] noted that cobalt-thorium combinations in continuous operation for 63 days lost only 10 per cent of their initial activity. Nevertheless, Fischer[141] has stated that the catalysts gradually become deactivated, probably due to recrystallization, i.e., the particles are thought to increase in size and there are then fewer points of catalytic activity. Furthermore, in all extended operations, the contact mass becomes saturated with a hard paraffin, which often loads the catalysts down to several times its own weight. Friedwald[142] asserts that this accumulation of paraffin apparently exerts no depreciatory effect on the activity of the mass. This statement, however, is contradictory to that of Fischer and Koch[143] who reported that the 10 per cent loss in activity of the cobalt-thorium mass just mentioned previously was completely restored by the extraction of the paraffin wax which had been deposited thereon. The regeneration process generally employed consists in dissolving the paraffin and treating the contact mass with nitric acid to dissolve the metals, filtering and reprecipitating.

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[136] British P. 452,417, 1936, to Studien- und Verwertungs-G.m.b.H.; *Brit. Chem. Abs.* **B**, 1936, 1031; *Chem. Abs.*, 1937, **31**, 1186. French P. 784,337, 1935; *Chem. Abs.*, 1936, **30**, 272.

[137] F. Fischer, *Oel, Kohle, Erdoel, Teer*, 1935, 11, 782; *J. Inst. Pet. Tech.*, 1935, **21**, 453A; *Chem. Abs.*, 1936, **30**, 3968; *Brit. Chem. Abs.* **B**, 1936, 51.

[138] M. Friedwald, *Rev. pétrolifère*, 1935, **634**, 733; *Chem. Abs.*, 1935, **29**, 5626; *Chem. Zentr.*, 1935, **2**, 1290; *Brit. Chem. Abs.* **B**, 1936, 1076.

[139] F. Fischer and K. Meyer, *Ges. Abhandl. Kenntnis Kohle*, 1934, **11**, 497; *Chem. Zentr.*, 1934, **2**, 1061; *Chem. Abs.*, 1935, **29**, 6747; *Brit. Chem. Abs.* **B**, 1935, 390.

[140] F. Fischer and H. Koch, *Brennstoff-Chem.*, 1932, **13**, 61; *Brit. Chem. Abs.* **B**, 1932, 376; *Chem. Abs.*, 1932, **26**, 2582.

[141] F. Fischer, *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 120; *J. Inst. Pet. Tech.*, 1935, **21**, 170A.

The catalytic material is packed into chambers around which, by means of jackets, a stream of oil is circulated. According to Friedwald,[144] temperatures of 190° to 195°C. are used for the cobalt-mixed type catalysts. The excess heat in the circulating oil is employed for generating steam. This utilization, which amounts to about 20 per cent of the heat of combustion of the initial feed gas, represents a considerable saving on the amount of fuel consumed.

In passage through the reactor a contraction of about 75 per cent of the initial volume of the gas is evidenced. After cooling the reaction mixture down to room temperature, it is introduced into a separator, from which the water and major portion of the liquid hydrocarbons are withdrawn. The hydrocarbon portion is subjected to distillation into four fractions: gases, liquids, applicable as motor fuels, higher-boiling liquids and a solid paraffin wax. Additional wax of a higher melting point is recovered from the catalyst. By passing the vapors leaving the separator through a tower filled with activated carbon (or adsorbent charcoal) the lower-boiling liquid hydrocarbons are stripped from the exit gases.

The primary products and the yields (in weight per cent) obtained in commercial operation have been given by Fischer[145] as:

Gasol (boiling below 30°C.)		8%
Gasoline (boiling range 30–125°C.)	37%	
" (" " 125–200°C.)	25%	
		62%
Lamp and Diesel oil (boiling over 200°C.)		24%
Solid paraffin wax from oil (melting point over 50°C.)		2%
Solid paraffin wax from catalyst (melting point over 100°C.)		4%
		100%

The proportion of liquids boiling in the gasoline range (30-200°C.), 62 per cent, amount to nearly two-thirds of the total. In addition, Diesel oil consitutes almost one-quarter of the total.

USES OF PRODUCTS OF THE CARBON MONOXIDE-HYDROGEN SYNTHESIS

No doubt the chief motivant instigating the majority of the numerous researches on the synthesis of higher hydrocarbons from carbon monoxide and hydrogen was the hope of attaining a synthetic motor fuel. In general, however, the gasoline obtained has a relatively low octane number, ordinarily about 47, according to Fischer.[146] But as Feldman[147] has pointed out, the complete absence of sulphur in the liquid product, Kogasin, makes the latter an ideal man-made petroleum stock.

[142] M. Friedwald, *loc. cit.*

[143] F. Fischer and H. Koch, *loc. cit.*

[144] M. Friedwald, *loc. cit.*

[145] F. Fischer, *Oel, Kohle, Erdoel, Teer,* 1935, 11, 782; *J. Inst. Pet. Tech.,* 1935, **21**, 453A; *Chem. Abs.,* 1936, **30**, 3968; *Brit. Chem. Abs.* **B**, 1936, 51.

[146] F. Fischer, *Oel, Kohle, Erdoel, Teer,* 1935, 11, 120; *J. Inst. Pet. Tech.,* 1935, **21**, 170A.

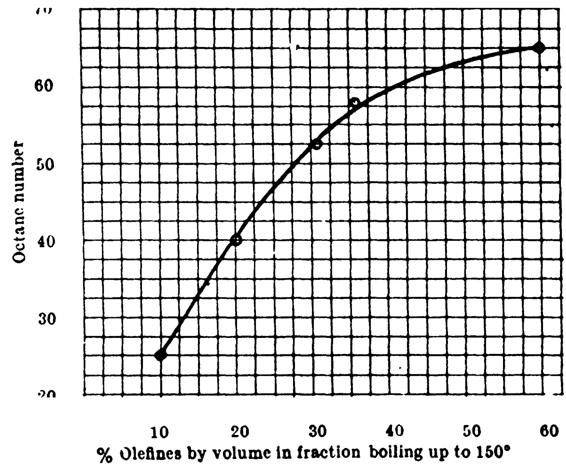
[147] O. Feldman, *S. African Mining Eng. J.,* 1935, **46** (1), 361; *Chem. Abs.,* 1935, **29**, 7055; *Brit. Chem. Abs.* **B**, 1936, 915.

He is of the opinion also that the only natural petroleums approaching the synthetic Kogasin in quality are those of the sulphur-free paraffin base type.

Gasoline. Myddleton and Walker[148] have discussed the characteristics of the synthetic gasoline (boiling up to 150°C.) fractionated from Kogasin. These investigators found that the octane number of this motor fuel increases greatly with the olefinic content, as is shown in Fig. 312. Thus, a liquid with 60 per cent of unsaturates, had an octane rating of 65 (C.F.R. motor method), whereas with one containing only 10 per cent, the octane value was only 25. It is therefore apparent that the olefinic content should be relatively high for possible utilization of this material as gasoline. Koch and Horn[149] have separated the lower-boiling Kogasin portion (below about 150°C., and having an octane number of 58) into 10°C. fractions and determined the antiknock rating and olefinic content of each cut. The lowest-boiling fraction contained 46 per cent unsaturates and had an octane number of 85, but for the highest-boiling portion the values dropped off to 23 per cent and 41.5 octane, respectively. For comparative purposes, an examination of a cracked gasoline (from natural petroleum) of substantially the same characteristics was made. The results of these tests showed that although the percentage of unsaturates in the different fractions of the latter was roughly constant, the antiknock rating also fell off with rising boiling point, but not as rapidly as with the synthetic mixture. According to Friedwald,[150] by blending the synthetic gasoline with benzene or with 10 to 20 per cent of alcohol, or by the addition of 0.05 per cent of lead tetraethyl, the octane number can be increased considerably, in the latter case to 80.

FIG. 312.
Effect of Olefin Content on Octane Rating of Synthetic Gasoline. (W. W. Myddleton and J. Walker)

Courtesy Society of Chemical Industry



Several proposals utilizing high pressure treatment have also been advanced for the manufacture of motor fuels from carbon monoxide and hydrogen. In most instances, the pressures are about 200 atmospheres and temperatures of 450-500°C., with catalysts of zinc oxide and chromic oxide.[151] Higher alcohols, however, are the main products of these reactions. By dehydration to olefins (with catalysts such as alumina at 300°C.), polymerization and hydrogenation, the latter may be converted into motor fuels. The reduction of carbon monoxide to liquid hydrocarbons under pressures of 20 atmospheres is also said to be effected in the presence of anthracene oil.[152]

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[148] W. W. Myddleton and J. Walker, *J.S.C.I.*, 1936, **55**, 121T; *Chem. Abs.*, 1936, **30**, 5393; *Brit. Chem. Abs.* **B**, 1936, 581; *J. Inst. Pet. Tech.*, 1936, **22**, 356A. Methods of increasing the olefinic content of Kogasin fractions have been outlined previously in this chapter.

[149] H. Koch and O. Horn, *Brennstoff-Chem.*, 1932, **13**, 164; *Brit. Chem. Abs.* **B**, 1932, 584; *Chem. Abs.*, 1932, **26**, 3657.

[150] M. Friedwald, *Rev. pétrolifère*, 1935, **634**, 733; *Chem. Abs.*, 1935, **29**, 5626; *Chem. Zentr.*, 1935, **2**, 1290; *Brit. Chem. Abs.* **B**, 1936, 1076.

Cracked Gasoline from Kogasin. Fischer[153] has suggested increasing the knock-resistance of the lower boiling Kogasin fraction by reforming[154] or cracking it to aromatic hydrocarbons. He states that high octane fuels are secured by cracking the higher boiling portions of Kogasin I (125° to 200°C.) Kogasin II (boiling over 200°C.) or even the wax material separated from the oil by cooling.[155]

Pichler[156] investigated the thermal conversion of the heavy oil (boiling from 240° to over 320°C., and corresponding to 10-20 per cent of the total oil produced in the synthesis) to unsaturated and aromatic hydrocarbons, using tubes 8 to 17 mm. in internal diameter, electrically heated to 500-700°C. Below 500°C., the reaction was quite slow, whereas above 600°C. gaseous olefins predominated. The yield of the latter rose rapidly with the temperature, from 20 per cent at 550°C. and a reaction time of 0.4 second to 62 per cent at 700°C. and 0.14 second. From 50 to 75 per cent of the oil was cracked into gaseous and low-boiling unsaturated and aromatic hydrocarbons, the remainder consisting of gaseous paraffins, unchanged oil and aromatic tar. By controlling the reaction time, no appreciable deposition to carbon is said to occur.

A study of the cracking of Kogasin II (boiling above 200°C.) has also been conducted by Peters and Winzer.[157] After removal of most of the solid paraffin, the stock had a specific gravity of 0.878; 57.6 per cent distilled between 200 and 300°C. A series of experiments was made cracking this material under various pressures. With temperatures below 560°C. (1040°F.), yields of liquid products from 50 to 80 per cent resulted. Aromatics, such as benzene, did not appear in the reaction mixture, however, unless the temperatures were in excess of 550°C. It was noted that at 530°C. and 80 atmospheres pressure, the quantity of gases produced could be reduced by about 75 per cent by tripling the rate of feed. Increase in pressure at constant temperature improved the yield of liquids, but with the same reaction time, more gases resulted. The cracked gasolines were highly unsaturated. Hydrogenation reduced their copper-dish gum values from 260 or 270 mg. to 43 mg. per 100 cc. However, the latter treatment also lowered the octane number to 48.5.

Incorporation of ethylene or cracked gas with the unsaturated gasoline obtained in the above tests was also investigated by Peters and Winzer,[158] using kieselguhr impregnated with phosphoric acid as catalyst. In one test, ethylene was charged into an autoclave to a pressure of 55 atmospheres, and heated to 330°C. After a few hours the pressure dropped from 270 to 100-150 atmospheres. Examination of the resultants indicated that ethylene alkylated the gasoline instead of polymerizing and the motor fuel obtained had an octane rating of 63.5. The investigators state that by cracking Kogasin II in the presence of a phosphoric acid catalyst, the yield of gasoline was increased from 21 to 30.6 per cent by volume.

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[151] For example, see British P. 448,690, 1936, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1936, 778; *Chem. Abs.*, 1936, **30**, 7837; *J. Inst. Pet. Tech.*, 1936, **22**, 401A. French P. 790,873, 1936; *Chem. Abs.*, 1936, **30**, 3206.

[152] British P. 449,274, 1936, to I. G. Farbenind. A.-G.; *J. Inst. Pet. Tech.*, 1936, **22**, 406A.

[153] F. Fischer, *Oel, Kohle, Erdoel, Teer*, 1935, 11, 120; *J. Inst. Pet. Tech.*, 1935, **21**, 170A.

[154] Reforming involves cracking of low octane gasolines or naphthas to increase the octane rating. See Chapter 3.

[155] Likewise, portions of the high-boiling oil may be cracked to form aromatics which can be added to the synthetic gasoline, thereby improving its antiknock rating. See British P. 354,215, 1930, to Ruhrchemie A.-G.; *Brit. Chem. Abs.* **B**, 1931, 1001; *Chem. Abs.*, 1932, **26**, 3904.

[156] H. Pichler, *Brennstoff-Chem.*, 1935, **16**, 404; *J. Inst. Pet. Tech.*, 1936, **22**, 45A; *Brit. Chem. Abs.* **B**, 1936, 51; *Chem. Abs.*, 1936, **30**, 3980.

[157] K. Peters and K. Winzer, *Brennstoff-Chem.*, 1936, **17**, 301; *Brit. Chem. Abs.* **B**, 1936, 966; *Chem. Abs.*, 1937, **31**, 1992.

[158] K. Peters and K. Winzer, *loc. cit.*

Diesel Oil. According to Fischer,[159] Kogasin II (boiling above 200°C.) makes an ideal Diesel fuel after the dissolved solid paraffins have been separated. Because of its high hydrogen content, it is said to give a somewhat higher mileage than the fuel from commercial gas oil.[160] Diesel oils of low pour points were made by Koch and Ibing[161] by cooling Kogasin II to temperatures of —10°, —20°, and —30°C. to remove the higher melting solid paraffins. The minimum yields of fuels with cloud points of the above temperatures obtained from this oil are given as 78, 62.5 and 45 per cent respectively.

Lubricating Oils. Although there are no fractions in Kogasin corresponding to the natural lubricating oils, Fischer[162] has enumerated three ways in which they can be synthesized. These are: (1) by condensing the lower boiling fractions, rich in olefins, with aluminum chloride. (2) by forming olefins from the saturated paraffins (such as by halogenation and subsequent dehalogenation) and catalytic condensation and (3) by condensing chlorinated fractions with aromatic hydrocarbons, according to the Friedel-Crafts reaction.

With regard to the first method, Fischer and Koch[163] suggested the use of Kogasin I, the low boiling fraction which contains about 35 per cent of unsaturates. Preparation of lubricants from Kogasin II, according to the second of Fischer's suggestions, has been discussed by Koch and Ibing.[164] These investigators point out that a uniform raw material is essential, and therefore subjected the oil to repeated fractionations at reduced pressure. By this treatment, isopentadecane was isolated from Kogasin II, and afterwards was chlorinated, mixed with about 10 to 15 per cent of the unchlorinated hydrocarbon and treated with 4 per cent of activated aluminum. The small quantities of aluminum chloride formed attack the alkyl chloride and cause hydrogen chloride to be evolved. The latter reacts with the metallic aluminum to form more aluminum chloride and this accelerates the rate of reaction. At 150°C., interaction followed three distinct courses. First, the catalyst caused cracking, as was evidenced by the presence of about 8 per cent of lower-boiling hydrocarbons (nonane and dodecane) in the product. Secondly, elimination of hydrogen chloride followed by intermolecular displacement of hydrogen led to the formation of the original hydrocarbon. Thirdly, polymerization and condensation were evidenced by the nature of the substances formed, which contained 1 double linkage and 1 or 2 naphthene rings.

The last method, a typical Friedel-Crafts reaction,[165] has been investigated by Fischer and Koch.[166] By chlorinating Kogasin II, substituted hydrocarbons containing up to 6 chlorine atoms were obtained. The latter were separated, mixed with about 1 to 3 volumes of an aromatic hydrocarbon (xylene, benzene, toluene, naphthalene, α-methylnaphthalene and also tetrahydronaphthalene were employed in these tests), and about 5 per cent of aluminum chloride, based on the weight of the chlorinated stock, added. Reaction began in the cold and was accelerated by stirring and warming on a water bath. The product was freed from the reaction mixture by washing, and was treated with a small quantity of fuller's earth, after which excess aromatic hydrocarbons and unreacted low boiling materials were removed by distillation. The lubricants are said to contain less than 0.1 per cent of chlorine and to have an average molecular weight of about 450. Those resulting from the trichloro Kogasin derivatives contained about 2 aromatic rings per molecule and had properties similar to those of an asphaltic base lubricating oil (such as Texas oil). No advantage was gained by using the more highly chlorinated fractions, as the condensates were too viscous.

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[159] F. Fischer, *Oel, Kohle, Erdoel, Teer,* 1935, **11**, 120; *J. Inst. Pet. Tech.*, 1935, **21**, 170A.

[160] R. Hartner-Seberich and H. Koch, *Brennstoff-Chem.*, 1932, **13**, 308; *Chem. Abs.*, 1932, **26**, 5733; *Brit. Chem. Abs.* **B**, 1932, 920.

[161] H. Koch and G. Ibing, *Brennstoff-Chem.*, 1935, **16**, 185; *J. Inst. Pet. Tech.*, 1935, **21**, 300A; *Brit. Chem. Abs.* **B**, 1935, 709; *Chem. Abs.*, 1936, **30**, 1984.

[162] F. Fischer, *loc. cit.*

[163] F. Fischer and H. Koch, *Brennstoff-Chem.*, 1933, **14**, 463; *J. Inst. Pet. Tech.*, 1934, **20**, 102A; *Brit. Chem. Abs.* **B**, 1934, 133; *Chem. Abs.*, 1934, **28**, 2513. See also British P. 453,973, 1935, to Studien- und Verwertungsgesellschaft m.b.H.; *Brit. Chem. Abs.* **B**, 1936, 1139; *J. Inst. Pet. Tech.*, 1936, **22**, 541A. French P. 792,021, 1935; *Chem. Abs.*, 1936, **30**, 4314.

[164] H. Koch and G. Ibing, *Brennstoff Chem.*, 1935, **16**, 261; *J. Inst. Pet. Tech.*, 1935, **21**, 411A; *Brit. Chem. Abs.* **B**, 1935, 889; *Chem. Abs.*, 1936, **30**, 1985.

[165] See Chapter 6. Also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**.

[166] F. Fischer and H. Koch, *Brennstoff-Chem.*, 1933, **14**, 463; *J. Inst. Pet. Tech.*, 1934, **20**, 102A; *Brit. Chem. Abs.* **B**, 1934, 133; *Chem. Abs.*, 1934, **28**, 2513.

Subsequent work by Koch and Ibing[167] on the aliphatic halide-aromatic condensation show that best results are obtained when the starting material is homogeneous, which can be brought about by repeated low pressure fractionation. The procedure advocated by these investigators is to mix monochloro-*n*-tetradecane containing about 10 per cent *n*-tetradecane with an equivalent weight of xylene and 10 per cent of its weight of aluminum chloride. The resulting lubricating oil (about 30 per cent yield) was water-white, with a blue fluorescence and had a specific gravity of 0.8610. The molecular weight corresponded not to tetradecylxylene, but to tridecylxylene, indicating the loss of a CH_2 group, which apparently had split off during the condensation. Similar experiments were repeated by Koch and Ibing in a study of the effect of milder conditions on the yield. But even with *n*-tridecane, benzene and only 5 per cent of aluminum chloride the reaction was violent and cooling with ice water was necessary. No low-boiling products of cracking were present in the reaction mixture, but the lubricating oil fraction (water-white with a bright bluish fluorescence) corresponded in its properties to dodecylbenzene, so that once more indications pointed to a splitting of a methylene group from the paraffin chain. Two higher boiling portions corresponding to the general formulas C_nH_{2n-8} and C_nH_{2n-14}, respectively, were also separated and found to have satisfactory viscosity-temperature coefficients. The latter substances are thought to have arisen from the union of benzene and dichlorinated paraffins which may have been present in the starting material. Koch and Ibing conclude that smaller proportions of aluminum chloride and temperatures below 100°C. give the optimum conversions to alkyl benzenes.

Fischer[168] has compared the properties of a winter grade commercial type motor oil with those of one made from Kogasin, as is shown in Table 233.

TABLE 233.—*Comparison of Commercial Motor Oil with Kogasin Lubricating Oil.*

	Winter Grade Commercial Motor Oil	Synthetic Kogasin Lubricating Oil
Sp.gr. at 20°C.	0.882	0.838
Viscosity at 20°C. (°Engler)	32.6	32.0
Viscosity at 50°C. (°Engler)	6.10	6.06
"Cold" Point, °C.	−16	−42
Flow Power[a] (U-tube method) mm. at −15°C.	3.5	over 30
Flow Power (U-tube method) mm. at −25°C.	0.0	" 30
Flash Point (open crucible), °C.	220	205

[a] See D. Holde, "Kohlenwasserstoffole und Fette," Julius Springer, Berlin, 1933, 414.

Fischer places the overall yield of lubricating oil from Kogasin as about 10 per cent of that of gasoline.

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[167] H. Koch and G. Ibing, *Brennstoff-Chem.*, 1935, **16**, 261; *J. Inst. Pet. Tech.*, 1935, **21**, 411A; *Brit. Chem. Abs.* **B**, 1935, 889; *Chem. Abs.*, 1936, **30**, 1985.

[168] F. Fischer, *Oel, Kohle, Erdoel, Teer*, 1935, **11**, 782; *J. Inst. Pet. Tech.*, 1935, **21**, 453A; *Brit. Chem. Abs.* **B**, 1936, 51; *Chem. Abs.*, 1936, **30**, 3968.

Other Uses. Fischer and Koch[169] have suggested converting the olefins of the "Gasol" portion into alcohol and utilizing the remaining gases as fuel. An alternative procedure is to heat Gasol to 1000°C. with short reaction times to produce illuminating gas and aromatic hydrocarbons.[170] The latter may be used for blending with the lower octane number motor fuel produced in the Kogasin synthesis. Polymerization of the olefinic constituents to form liquids of the "polymer gasoline" type[171] by treatment with catalysts such as phosphoric acid, zinc chloride and boron trifluoride has also been suggested.[172]

Paraffin wax separated from Kogasin' II is adapted for the manufacture of candles, and because of its high purity, can also be employed as an intermediate for the production (by oxidation) of carboxylic acids.[173] The hard paraffin wax (so-called "Ceresin") removed from the catalyst has good dielectric properties and is therefore applicable as electrical insulation. According to Graefe,[174] a synthetic ceresin (melting point 96°C.) is much more difficultly liquefied by the addition of solvents than is the natural ceresin, paraffin or montan wax.

ECONOMICS OF THE KOGASIN PROCESS

The extensive equipment adapted to the requirements of large scale operation in the United States demands an installation cost not in keeping with a country still possessing vast supplies of natural petroleum. For those countries which seek to be self-sustaining in all respects there may be some justification, on nationalistic grounds, for the erection of Fischer units. But as yet such a process apparently cannot well compete with natural petroleum, both as to cost of production and with respect to the octane value of the gasoline fuel obtained.[175]

[169] F. Fischer and H. Koch, *Brennstoff-Chem.*, 1932, **13**, 428; *Brit. Chem. Abs.* **B**, 1933, 50; *Chem. Abs.*, 1933, **27**, 2017.

[170] British P. 354,215, to Ruhrchemie A.-G.; *Brit. Chem. Abs.* **B**, 1931, 1001; *Chem. Abs.*, 1932, **26**, 3904.

[171] See Chapter 26.

[172] British P. 454,389, 1935, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* **B**, 1936, 1190; *J. Inst. Pet. Tech.*, 1936, **22**, 541A. French P. 800,956, 1936; *Chem. Abs.*, 1937, **31**, 242.

[173] O. Feldman, *S. African Mining Eng. J.*, 1935, **46** (1), 361; *Chem. Abs.*, 1935, **29**, 7055; *Brit. Chem. Abs.* **B**, 1936, 915. M. Friedwald. *Rev. pétrolifère*, 1935, **634**, 733; *Chem. Abs.*, 1935, **29**, 5626; *Chem. Zentr.*, 1935, **2**, 1290; *Brit. Chem. Abs.* **B**, 1936, 1076.

[174] E. H. E. Graefe, *Öle, Wachse, Seife, Kosmetik*, **1936** (13), 1; *Chem. Abs.*, 1937, **31**, 241. *Petroleum Z.*, 1936, **32** (37), 5; *Brit. Chem. Abs.* **B**, 1936, 1026.

[175] According to M. Friedwald (*Rev. pétrolifère*, 1935, **634**, 733; *Chem. Abs.*, 1935, **29**, 5626; *Chem. Zentr.*, 1935, **2**, 1190; *Brit. Chem. Abs.* **B**, 1936, 1076), the price of the initial investment in the Fischer process is less than that of the Bergius method, which involves the direct hydrogenation of coal. (The principles underlying the latter type of operation have been discussed by Carleton Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., Inc., New York, **1930**.) The construction cost in France for a Kogasin unit capable of producing 25,000 tons of gasoline per annum is estimated at 40 million francs (*Chem. Trade J.*, 1936, **98**, 286; *J. Inst. Pet. Tech.*, 1936, **22**, 265A).

Chapter 53

Petroleum Hydrocarbons in Anesthesia

Although anesthesia is most often induced by ether or by various local anesthetics, such as the *p*-aminobenzoates, some gases are being used quite widely for a general narcosis. For example, a number of the hydrocarbon gases, including ethylene, acetylene and cyclopropane, have also found application in this field.[1] The anesthetic effect of gasoline vapors was described in 1920 by Haggard.[2] He observed that, although the vapors possessed an anesthetic action somewhat like diethyl ether, they also had marked convulsant properties. This was considered to appertain to the same stage of anesthesia as is marked by excitement during the administration of ether. Haggard also showed that the stage of full anesthesia was quite narrow, that is, shortly after unconsciousness ensued, the vapors were toxic. The toxicity of gasoline vapors was not, however, in any sense as great as that of the carbon monoxide produced by incomplete combustion in a gasoline engine.

Brown and Henderson[3] have observed that the alkanes (methane and propane) cause complete anesthesia only in such large concentration (90 to 93 per cent) that there are cardiac irregularities and a drop in blood pressure. Pentane possesses narcotic properties also, but the anesthetic and toxic doses are very near together.

Butane is reported to have less anesthetic activity and lethality than pentane. Also, branched isomers of each of these hydrocarbons are said to be less active than the straight-chain compounds.[4] Experiments with rats and with humans have indicated that natural gas in concentrations up to 30 per cent in air has no apparent effect on the body functions.[5] However, concentrations of 60 and 80 per cent in oxygen caused the animals to lose muscular control to some extent and to assume a state resembling drunkenness. Recovery was very quick on restoration to air and no after effects were noted.

ETHYLENE AS AN ANESTHETIC

In 1923, Luckhardt and Carter[6] investigated the physiologic effect of ethylene on dogs and also on men. They reported that a deep surgical anesthesia was rapidly produced and that analgesia came on very early. There was said to be no apprehension of asphyxia and very few symptoms, such as nausea and cyanosis, which might cause danger or discomfort. By using mixtures of ethylene and oxygen it was shown that narcosis results from the former, and that the asphyxial phenomena produced by the undiluted gas are due to the lack of oxygen. Subsequently a report was made of the result of employing ethylene in 106 surgical cases.[7] In these, difficulty was encountered in only two cases, in which surgical anesthesia could not be induced. Luckhardt and Carter noted the advantages which ethylene had over nitrous oxide and diethyl ether. Their results were confirmed by Brown and Henderson[8] who also noted that toxic doses caused failure of respiration and the vasomotor center, and that the cardiac death was due to asphyxia.

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[1] The action of acetylene, ethylene, propene and butene on various insects and on plants has been investigated by P. W. Zimmerman, *Contr. Boyce Thompson Inst.*, 1935, **7**, 147; *Chem. Abs.*, 1935, **29**, 7005.

[2] H. W. Haggard, *J. Pharmacol.*, 1920, **16**, 401; *Chem. Abs.*, 1921, **15**, 1944. *Cf.* also A. I. Brusilovskaya, *Arch. intern. pharmacodynamic*, 1936, **52**, 289; *Chem. Abs.*, 1936, **30**, 6450.

[3] W. E. Brown and V. E. Henderson, *J. Pharmacol.*, 1926, **27**, 1; *Chem. Zentr.*, 1926, 1, 3082; *Chem. Abs.*, 1926, **20**, 1869.

[4] R. W. Stoughton and P. D. Lamson, *J. Pharmacol.*, 1936, **58**, 74; *Chem. Abs.*, 1937, **31**, 465; *Brit. Chem. Abs.* A, 1936, 1552.

[5] D. R. Drury, *Gas*, 1936, **12** (9), 32; *Gas Age-Record*, 1936, **78**, 295; *Chem. Abs.*, 1936, **30**, 7700.

[6] A. B. Luckhardt and J. B. Carter, *J. Am. Med. Assoc.*, 1923, **80**, 765; *Chem. Abs.*, 1923, **17**, 2006.

According to Lundy[9] ethylene could be used advantageously in nearly all types of surgical risks. He stated that it had less effect on cardiovascular balance than other local and general anesthetics which were commonly employed. Among other advantages which have been noted for ethylene[10] are ease of induction, rapid recovery, absence of sweating and of respiratory irritation. As a result of 521 cases in which it was used, Brumbaugh[11] found that one of the disadvantages was that there was somewhat greater tendency for the oozing of wounds than with other anesthetics, although this stopped when the gas-supply was withdrawn.

Ethylene has been employed successfully in special fields. Thus, it has been used with good results in obstetrics,[12] in which it is said to be superior to diethyl ether or nitrous oxide.[13] On the other hand, Gwathmey reports that the anesthetic value of ethylene seems to fall between nitrous oxide and ether.[14] He believed that premedication with Epsom salts and morphine was desirable.

In dental surgery there has been some application of this unsaturated hydrocarbon. Moravec[15] believed it of value in cases where there is chronic hypertension and that it may be used simultaneously with nitrous oxide to promote relaxation. On the other hand there was some danger if anoxemia (lack of oxygen in the blood) occurred without cyanosis.[16] However, Selden[17] observed that there was some danger of asphyxia or explosion when using ethylene with other gases such as carbon dioxide or oxygen. On the other hand Christiansen[18] recommended a mixture containing 10 per cent oxygen and 90 per cent ethylene as a general anesthetic in dentistry. In cases in which the time for operative working was more than 5 minutes, the proportion of oxygen in the mixture could be raised to 20 per cent or more. He reports much the same results as were obtained in the cases mentioned previously, that is, anesthesia was readily effected and maintained, recovery was rapid and there was no excitement either during induction or recovery. Muscular relaxation was produced without cyanosis. There was no respiratory irritation, excessive perspiration or post-operative disturbance, and nausea occurred only rarely.

One of the dangers which is attendant upon the use of ethylene and mixtures in which it is a component is the explosive nature of the hydrocarbon gas when admixed with oxygen or air. This danger was recognized by the users, and appropriate precautions were taken. Brown[19] has tended to minimize this danger by showing that it requires 40 to 45 per cent pure oxygen or 90 per cent air (about 21 per cent oxygen) in mixture with ethylene to reach explosive proportions. Ordinarily but 10 to 25 per cent of oxygen is used in the anesthetic mixture. He further observed that it would require about 6 hours of continuous anesthesia for ethylene from the spill valve to produce an explosive mixture in a room 15 feet square and 12 feet high. Luckhardt[20] points out that there is some possibility of igniting ethylene-oxygen mixtures by hot cauteries or by static sparks. He observed that there was the same danger in using ether-oxygen or ether-nitrous oxide-oxygen mixtures and that the equipment in the operating room must be so designed as to prevent such an occurrence.

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[7] A. B. Luckhardt and J. B. Carter, *J. Am. Med. Assoc.*, 1923, **80**, 1440; *Chem. Abs.*, 1923, **17**, 2751.

[8] W. E. Brown and V. E. Henderson, *Arch. intern. pharmacodynamie*, 1923, **28**, 257; *Chem. Abs.*, 1924, **18**, 2760. See also V. E. Henderson, *Can. Med. Assoc. J.*, 1927, **17**, 1158; *Chem. Abs.*, 1928, **22**, 266.

[9] J. S. Lundy, *J. Am. Med. Assoc.*, 1924, **83**, 350; *Chem. Abs.*, 1924, **18**, 3220.

[10] A. B. Luckhardt and D. Lewis, *J. Am. Med. Assoc.*, 1923, **81**, 1851; *Chem. Abs.*, 1924, **18**, 1153. See also A. B. Luckhardt, *ibid.*, 1924, **83**, 2060; *Chem. Abs.*, 1925, **19**, 1162. G. A. Johnstone, *Am. Med.*, 1927, **33**, 367; *Chem. Abs.*, 1927, **21**, 3967. H. Cabot and H. K. Ransom, *Ann. Surgery*, 1927, **86**, 255; *Chem. Abs.*, 1927, **21**, 3697. J. T. Gwathmey, M. H. Feldman, *Dental Cosmos*, 1930, **72**, 1164; *Chem. Abs.*, 1931, **25**, 2484; *Chem. Zentr.*, 1931, 1, 1638. H P. Fairlie, *Brit. J. Anesth.*, **1928**, 154; *Quart. J. Pharm.*, 1928, 1, 476; *Chem. Abs.*, 1929, **23**, 3974.

[11] J. D. Brumbaugh, *Military Surgeon*, 1928, **63**, 32; *Chem. Abs.*, 1928, **22**, 3697.

[12] J. Kreiselman and H. F. Kane, *Surgery, Gynecol. Obstetrics*, 1936, **43**, 389; *Chem. Abs.*, 1926, **20**, 3740.

[13] N. S. Heany, *J. Am. Med. Assoc.*, 1924, **83**, 2061; *Chem. Abs.*, 1925, **19**, 1162.

[14] J. T. Gwathmey, *Arch. Surg.*, 1925, **10**, 568; *Chem. Abs.*, 1925, **19**, 1312.

[15] E. L. Moravec, *J. Am. Dental Assoc.*, 1927, **14**, 671; *Chem. Abs.*, 1927, **21**, 2320.

[16] Cyanosis is a pale-blue discoloration of the skin which is due to the circulation of imperfectly oxygenated blood. It is sometimes called blue jaundice.

[17] H. M. Selden, *Dental Cosmos*, 1931, **73**, 454; *Chem. Abs.*, 1931, **25**, 3127.

[18] J. F. Christiansen, *Dental Cosmos*, 1924, **66**, 346; *Chem. Abs.*, 1924, **18**, 1337.

A method for eliminating the danger of explosions due to static sparks has been proposed by Lewis and Boehm.[21] All the objects in the immediate range of the operating table are grounded, as well as the persons about the table and the patient. The reducing valve on the tank and the mixing chamber are connected by a wire. Both ends of the breathing tube are connected by means of a bare wire running inside the tube. A moist cloth establishes contact between the metal of the mask and the patient's face, and a light brass chain runs from his arm to the metal part of the table. An insulated wire connects the table with the machine which is grounded by means of a heavy moist cloth. The anesthetist and other persons present stand on a large moist bath mat which is grounded. In this way there should be no danger of the formation of any sparks which could cause an explosion.

According to Poe[22] elimination of hazard due to sparks is effected by causing rebreathing of the ethylene mixture which is added after unconsciousness is first brought about using nitrous oxide and oxygen. After five or six breaths are exhaled into the rebreathing bag the relative humidity is 100 per cent, and, since 55 to 65 per cent humidity will dispel static electricity, there is said to be no danger under these conditions.

As has been stated earlier in this chapter, the use of ethylene alone is likely to cause asphyxia, and it is consequently the customary practice to employ ethylene and oxygen simultaneously. As a result of experiments carried out on rats, rabbits, dogs and other animals, Goldman found[23] that anesthesia did not occur until there was 12 per cent or less oxygen with the ethylene. He also noted that the content of oxygen could be as high as 20 or 30 per cent when acetylene was substituted for the olefin. Other mixtures, such as acetylene-nitrous oxide-oxygen and acetylene-ethylene-oxygen were tried and were fairly satisfactory agents. Parker and McDonald[24] have studied the application of mixtures containing ethylene, nitrous oxide and oxygen. When the gases were rebreathed with no filter to remove the carbon dioxide which was exhaled, the oxygen concentration remained practically constant and the average concentration of ethylene was slightly higher than that of the nitrous oxide. On the other hand, when a carbon dioxide filter was present, there was a gradual accumulation of oxygen and the average concentration of nitrous oxide was the higher. It is interesting to note that Kleindorfer[25] has reported that 5 to 10 per cent of carbon dioxide has an additive effect on the anesthesia produced by subanesthetic concentrations of ethylene.

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[19] W. E. Brown, *J. Am. Med. Assoc.*, 1924, **82**, 1039; *Chem. Abs.*, 1924, **18**, 1713. *Cf.* also J. Blomfield, *Proc. Roy. Soc. Med.*, 1926, **19**, Sect. Anesthetics, 39; *Chem. Abs.*, 1927, **21**, 961; *Ber. Ges. Physiol.*, 1926, **39**, 145; *Chem. Zentr.*, 1927, **2**, 455.

[20] A. B. Luckhardt, *J. Am. Med. Assoc.*, 1924, **82**, 1603; *Chem. Abs.*, 1924, **18**, 2762. See also C. H. Davis, *ibid.*, 1607; *Chem. Abs.*, 1924, **18**, 2762.

[21] W. B. Lewis and E. F. Boehm, *J. Am. Med. Assoc.*, 1925, **84**, 1417; *Chem. Abs.*, 1925, **19**, 2565.

[22] J. G. Poe, *J. Am. Med. Assoc.*, 1935, **105**, 66.

[23] J. L. Goldman, *Dental Cosmos*, 1928, **70**, 920; *Chem. Abs.*, 1928, **22**, 4645.

[24] F. P. Parker and R. McDonald, *Arch. Surg.*, 1931, **22**, 1034; *Chem. Abs.*, 1931, **25**, 5211.

[25] G. E. Kleindorfer, *J. Pharmacol.*, 1931, **43**, 445; *Chem. Abs.*, 1932, **26**, 2519; *Chem. Zentr.*, 1932, **1**, 1553. *Proc. Soc. Exptl. Biol. Med.*, 1931, **28**, 924; *Chem. Zentr.*, 1932, **2**, 3737.

In this connection also the technique of rebreathing a gas mixture should be mentioned. The essential feature of this method is that the same mixture of gases is used throughout the period of anesthesia.[26] Carbon dioxide is removed with the aid of a canister of soda-lime and oxygen is supplied continuously to replace that used by the patient. Changes in composition of the mixture are effected by the anesthetist by admitting either oxygen or anesthetic as required. One advantage of this method is the economy of anesthetic. This permits the use of a more expensive anesthetic without prohibitive cost to the patient. Furthermore there is less contamination of the air breathed by the surgeon and assistants, and less danger of the formation of explosive mixtures in the air of the room. For example, cauteries may be performed if sufficient care has been exercised in freeing the anesthetic mask from leaks. This is also of advantage in experimental work, Waters,[27] for example, having reported that by use of this technique he was able to use trimethylethylene as an anesthetic in more or less duplication of Snow's work.

Ethylene in conjunction with still other compounds has been proposed as an anesthetic. Thus, Cheney[28] suggested that the olefin be mixed with 0.5 to 5.0 per cent of ether vapor. The gases may be liquefied under 1000 pounds pressure or more. Ethylene has been used successfully in conjunction with avertin (tribromoethanol).[29] In this instance, however, it was found that the power of the blood to combine with carbon dioxide was slightly decreased, and the sugar-content of the blood was slightly increased.

ANALYSIS OF ETHYLENE FOR ANESTHESIA

A gas intended for use in anesthesia cannot be too pure when employed on human patients. The report of Sherman, Swindler and McEllroy[30] of deaths from carbon monoxide poisoning after ethylene anesthesia showed the dangers inherent in a product of uncertain purity. Many tests for impurities have been investigated by The Medical Association Laboratory and those which are considered of importance are:[31] the behavior of the gas toward methyl red and absence of carbon dioxide (tested with barium hydroxide), acetylene, phosphine, aldehydes and hydrogen sulphide (tested with ammoniacal silver nitrate). The proportion of ethylene is determined by absorption in bromine water. Oxygen and carbon monoxide may be determined by absorption in alkaline pyrogallol and an ammoniacal or hydrochloric acid solution of cuprous chloride, respectively. In samples from two manufacturers whose products were accepted, the methyl red, ammoniacal silver nitrate and barium hydroxide tests were all negative. The results are shown in Table 234 where Samples 1 and 3 are from one and 2 and 4 from the other producer.

The methods which have been recommended for the analysis of ethylene by Busi and Collina[32] differ from those used by the A.M.A. Laboratory in shaking the reagent and gas rather than bubbling the gas through the reagent. In testing for carbon dioxide the gas is sampled in a bulb of approximately 500 cc. capacity. To

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[26] R. M. Waters, *California and Western Medicine*, 1931, **35**. D. E. Jackson, *J. Lab. Clin. Med.*, 1915, **1**, 1; *Chem. Abs.*, 1916, **10**, 484.

[27] R. M. Waters, *Proc. Roy. Soc. Med.*, 1936, **30**, 11.

[28] M. H. Cheney, U. S. P. 1,712,250, May 7, 1929, to Cheney Chemical Co.; *Chem. Abs*, 1929, **23**, 3307; *Brit. Chem. Abs.* **B**, 1929, 699; *Chem. Zentr.*, 1929, **2**, 602.

[29] H. A. Widenhorn, *Ann. Surgery*, 1931, **94**, 892; *Chem. Abs.*, 1932, **26**, 1337; *Chem. Zentr.*, 1932, **1**, 2863.

[30] W. O. Sherman, C. H. Swindler and W. S. McEllroy, *J. Am. Med. Assoc.*, 1926, **86**, 1765.

[31] Report by A.M.A. Chemical Laboratory, *J. Am. Med. Assoc.*, 1927, **88**, 322; *Chem. Abs.*, 1927, **21**, 1520.

[32] M. Busi and C. Collina, *Atti soc. ital. progresso sci.*, 1931, **19** (2), 195; *Chem. Abs.*, 1932, **26**, 1707.

TABLE 234.—*Composition in Per Cent of Ethylene for Anesthesia.*

Sample	Ethylene	Residual Gases	Oxygen	Carbon Monoxide
1	99.37	0.63	0.13	0.00
2	99.42	0.58	0.58	0.00
3	99.15	0.85	0.18	0.00
4	98.93	1.07	0.23	0.00

the flask is added 5 cc. of a saturated solution of barium hydroxide. A precipitate should form on agitation if there is 1 part of carbon dioxide to 5000 of ethylene. Similarly, a solution of 1 or 2 drops of methyl red in 5 cc. of distilled water is shaken with the sample. There should be no acid reaction.

Acetylene forms a white precipitate when a sample of ethylene (containing as little as 1 part in 20,000) is shaken with an alkaline solution of potassium mercuric iodide. This precipitate blackens in the presence of phosphine, arsine or stibine. An ammoniacal solution of silver nitrate will react with carbon monoxide, acetylene, phosphine, arsine, formaldehyde and hydrogen sulphide.

The presence of carbon monoxide may be shown and estimated quantitatively by means of a test employing pyrogallic and tannic acids. About 250 cc. of the gas (under investigation) is shaken with 2.5 parts diluted guinea-pig blood (1 part blood to 20 of water) in a container. The blood is then run into a small test tube and 0.04 g. of a mixture of equal parts pyrogallic and tannic acids is added. The tube is permitted to stand at least ½ hour after shaking the contents. If the precipitate is gray-brown, carbon monoxide is present in less than 0.01 per cent; if the precipitate is red, the intensity of the color is proportional to the amount of monoxide present.

EFFECT OF ETHYLENE AS AN ANESTHETIC

In connection with the use of an anesthetic, the effect upon the composition and characteristics of the blood must receive some attention. One of the most pronounced features of the blood is its slightly alkaline reaction (*p*H 7.39), which is protected by buffers in the blood plasma. There is present a considerable amount of buffers to protect the blood during heavy exercise when quite large quantities of lactic acid may be formed. The alkali available in the blood for buffering is spoken of as the alkaline reserve. A decrease in this reserve is an acidosis even if the blood still maintains its normal *p*H value. Anesthesia has an effect on the blood which depends upon the substance used as an anesthetic. According to Leake[33] ether and chloroform cause a lowering of the blood *p*H while nitrous oxide and oxygen bring about an initial alkalemia (blood alkalinity) which gradually tends toward an acidemia (blood acidity). The effect of ethylene-oxygen anesthesia depends upon whether or not there is a lack of oxygen in the blood (anoxemia). When there is, the result is said to be practically the same as in nitrous oxide-oxygen anesthesia. Without anoxemia there is a lowering of the *p*H which is not beyond normal limits after 40 minutes of anesthesia.

Oberhelman and Dyniewicz[34] reported that ethylene-oxygen anesthesia caused less decrease in the alkaline reserve than that induced by ether, chloroform or nitrous oxide, and there was no approach to a dangerously low level in any uncomplicated cases. Ethylene-ether apparently had a somewhat greater disturbing action than ethylene-oxygen. It was also noted that the effect on blood sugar was slight.

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[33] C. D. Leake, *J. Am. Med. Assoc.*, 1924, **83**, 2062; *Chem. Abs.*, 1925, **19**, 1162.

[34] H. A. Oberhelman and H. A. Dyniewicz, *J. Am. Med. Assoc.*, 1924, **83**, 2012; *Chem. Abs.*, 1925, **19**, 1162.

and no changes which exceeded the normal variation were observed in the non-protein nitrogen content (urea) of the blood. The changes in blood pressure were more similar to those brought about by normal sleep than when anesthesia was induced by ether, chloroform or nitrous oxide.

In tests conducted upon diabetics protected by insulin, Lehmann[35] observed there was no post-operative acidosis in cases where there was a high or low blood sugar level. In fact, the post-operative plasma carbon dioxide value was said not even to approach an acidosis.

A study of the effects produced by ethylene-oxygen anesthesia in normal subjects has been reported by Brumbaugh.[36] Fifteen subjects were anesthetized for 1 hour without premedication and without operative or other complicating factors. No changes were observed in the hemoglobin, icterus index,[37] coagulation time of the blood, character of the blood clot, urine or pulse rate. Slight increases were observed in blood sugar and in the systolic blood pressure. No increase in the blood urea was noticed immediately after anesthesia, but an increase averaging 18.7 per cent was noted 24 hours afterwards. There was a slight but temporary acidosis. Comparable results are given by Trout[38] who found, in addition to the effects on blood sugar and coagulation time which were observed by other workers, that there was only a slight disturbance of the native complement of the blood.[39] In working on dogs which had been held under ethylene anesthesia for 20 minutes, he observed increase in both blood sugar and native complement and decreases in coagulation and bleeding times. The changes, however, were less than when other anesthetics were used.[40]

Another of the effects of various anesthetic gases which has been studied is the change in the osmotic resistance of the erythrocytes (red blood cells) to hypotonic fluids.[41] It was observed that chloroform caused a marked lowering of the resistance of the red blood cells of a dog while carbon dioxide had the reverse effect. There was an apparent increase after 10 minutes of ether anesthesia although the resistance of the red blood cells was much lower than normal after 30 minutes anesthesia. Either nitrous oxide or ethylene with oxygen caused a slight reduction in osmotic resistance, but even after an hour it was not so low as was found for either ether or chloroform. When ethylene was employed without oxygen and after 20 minutes the animal brought to asphyxiation, the osmotic resistance of the red cells was considerably reduced for 0.4 per cent hypotonic Simmel's fluid but only slightly below normal for the higher dilutions (0.6 and 0.7 per cent). Experiments by Niclous and Yovanovitch have shown[42] that from 70 to 80 per cent of the ethylene which is dissolved in the blood during anesthesia is present in the red cells, the remainder being in the plasma. This indicates that ethylene has slightly less affinity for the erythrocytes than chloroform and about as much as ethyl chloride. The relative distribution was observed both during anesthesia *in vivo* and *in vitro*. The total amount of ethylene in the blood depends upon its concentration in the inhaled air. It varies, for example, between 8 and 10 cc. per 100 cc. of blood as the concentration in the inhaled gas ranges between 65 and 77 per cent. When the amount of ethylene is less than 50 per cent of the inhaled gas, there may be a decided increase in the carbon dioxide content of the blood.

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[35] I. I. Lehmann, *Anesthesia and Analgesia*, 1931, **10**, 142; *Chem. Abs.*, 1931, **25**, 4063.

[36] J. D. Brumbaugh, *J. Am. Med. Assoc.*, 1928, **91**, 462; *Chem. Abs.*, 1928, **22**, 4175.

[37] The icterus index is a measure of the bilirubin content of the blood. It is expressed as a coefficient of dilution. One cc. of clear plasma is diluted until the color matches a solution of 0.05 g. potassium dichromate in 500 cc. of water to which have been added two drops of dilute sulphuric acid. E. Meulengracht, *Ugeskrift for Laeger*, 1919, **81**, 1785; *J. Am. Med. Assoc.*, 1920, **74**, 68; *Chem. Abs.*, 1920, **14**, 572; *Compt. rend. soc. biol.*, 1921, **84**, 153; *Chem. Zentr.*, 1921, **2**, 584; *Chem. Abs.*, 1922, **16**, 1443; *Deut. Arch. klin. Med.*, **1921**, 38; *Chem. Abs*, 1922, **16**, 3916.

[38] H. H. Trout, *Ann. Surgery*, 1927, **86**, 260; *Chem. Abs.*, 1927, **21**, 3967.

[39] The native complement of the blood is a term used to denote certain of the substances of uncertain composition which have an enzymatic nature.

[40] H. H. Trout, *Anesthesia and Analgesia*, 1929, **8**, 269; *Chem. Abs.*, 1930, **24**, 428. *Cf.* also E. T. Conybeare, H. B. Densham, M. Maizels and M. S. Pembrey, *Proc. Physiol. Soc.*, *J. Physiol.*, 1927, **64**, xix; *Chem. Abs.*, 1928, **22**, 817. D. C. Strauss and H. H. Rubin, *J. Am. Med. Assoc.*, 1927, **88**, 310; *Chem. Abs.*, 1927, **21**, 1851. Also the work on water absorption of frogs by H. W. Neild and A. F. Serritella, *Am. J. Physiol.*, 1934, **108**, 550; *Chem. Abs.*, 1934, **28**, 6205.

[41] When aqueous solutions of lower osmotic pressure than the blood plasma (hypotonic fluids) are permitted to act on the erythrocytes, a part of the latter absorb so much water by diffusion that they rupture. This is known as hemolysis. The reverse process, i.e., shriveling of the red blood cells, takes place in the presence of a solution of higher osmotic pressure than the blood plasma (a hypertonic solution). Solutions which have the same osmotic pressure as the blood are said to be isosmotic or isotonic. C. D. Leake, C. Backus, H. Burch and K. O'Shea, *Proc. Soc. Exptl. Biol. Med.*, 1927, **25**, 92. C. D. Leake, H. Lapp, J. Tenney and R. M. Waters, *ibid.*, 93, 94; *Chem. Abs.*, 1928, **22**, 2616.

Lazarev[43] has found that some narcotics are more soluble in water than in blood and others have reverse solubilities. From this he concludes that some of the narcotic is present in combination with a portion of the blood and is not truly dissolved. The values of the ratio of the bound narcotic to the water-dissolved portion are shown in Table 235.

TABLE 235.—*Ratio of Dissolved to Bound Solute.*

Substance	Ratio	Substance	Ratio
Nitrogen	0.13	Methane	0.5
Nitrous oxide	0.2	Acetylene	0.2 to 0.3
Ethyl chloride	0.8 to 2	Ethylene	0.8 to 1.25
Chloroform	3.3	Benzene	0.8
Diethyl ether	0.2	Cyclohexane	4.4
Pentane	11.	Hexane	22.
Heptane	53.5		

He reported that strong narcotics are probably completely in the bound condition in the blood.

The effect of ethylene on various organs of the body has received some attention. Walton[44] has shown, for example, that varying degrees of ethylene or ether anesthesia for times up to 1 hour had no effect on the 24-hour urinary output. Rosenthal and Bourne[45] observed that when nitrous oxide and ethylene were administered through a mask there was no resultant disturbance of the liver. On the other hand, when given in a closed chamber with poor oxygenation, both immediate and delayed hepatic disorders resulted. The consequences were far more severe when chloroform was used and somewhat more so when ether was administered. In the former case after 30 minutes anesthesia, eight days were required for recovery, while in the latter a day was usually sufficient. The bromosulphalein test[46] showed disturbances of the liver's function for some time after pigment metabolism had returned to normal. The effect of ethylene anesthesia on the stomach was investigated by Johnston and Ivy.[47] They found that gastric secretion was less depressed by ethylene than by ether. Emptying of the stomach by ethylene was delayed through loss of motion or because of closing of the outlet of the stomach by contraction of the pylorus.

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[42] M. Niclous and A. Yovanovitch, *Compt. rend soc. biol.*, 1925, **93**, 1653, 1657; *Chem. Abs.*, 1926, **20**, 2207; *Chem. Zentr.*, 1926, **1**, 2217. *Cf.* M. Niclous, *ibid.*, 1650; *Chem. Zentr.*, 1926, **1**, 2217.

[43] N. V. Lazarev, *J. Physiol. (U.S.S.R.)*, 1936, **20**, 939; *Chem. Abs.*, 1936, **30**, 7683.

[44] R. P. Walton, *J. Pharmacol.*, 1933, **47**, 141; *Chem. Abs.*, 1933, **27**, 3253. *Cf. Proc. Soc. Exptl. Biol. Med.*, 1932, **29**, 1072; *Chem. Zentr.*, 1933, **2**, 1393.

[45] S. M. Rosenthal and W. Bourne, *J. Am. Med. Assoc.*, 1928, **90**, 377; *Chem. Abs.*, 1928, **22**, 2006.

[46] The bromosulphalein test depends upon the fact that, whereas this dyestuff is very rapidly excreted by the normal liver, it remains in the blood for some time if there is any hepatic injury. The dyestuff is determined in the blood colorimetrically. S. M. Rosenthal and E. C. White, *J. Pharmacol.*, 1924, **24**, 265; *Chem. Abs.*, 1925, **19**, 357. *J. Am. Med. Assoc.*, 1925, **84**, 112.

[47] R. L. Johnston and A. C. Ivy, *Am. J. Physiol.*, 1926, **78**, 104; *Chem. Abs.*, 1926, **20**, 3510. *Cf.* also G. H. Miller, *J. Pharmacol.*, 1926, **27**, 211; *Chem. Abs.*, 1926, **20**, 1869; *Chem. Zentr.*, 1926, **1**, 3082.

PROPENE AND ITS HOMOLOGUES AS ANESTHETICS

One of the earliest reported uses of a hydrocarbon to induce anesthesia is the statement that Snow used amylene on 238 patients in the middle of the nineteenth century.[48] Since that time very few of the alkenes have been so employed to any extent. In 1924, Brown[49] stated that propene possessed anesthetic properties and, in concentrations as low as 37 per cent, when mixed with either oxygen or air was capable of inducing anesthesia. The concentration of hydrocarbon which was necessary to maintain anesthesia was even less and varied from 20 to 31 per cent. It was observed, however, that when the proportion of olefin was above 65 per cent it was more or less poisonous, toxic symptoms appearing in 2 minutes when mixtures containing more than 70 per cent propene were used.

In the following year, Riggs[50] reported the anesthetic actions of the lower members of the alkene series. It was noted that ethylene and propene, unlike butene and pentene (amylene), caused no nervous symptoms or excitement stage. Light anesthesia was induced in white rats of 100 to 150 g. weight in from 15 to 22 minutes by mixtures containing 90, 40, 20 and 6 per cent, respectively, of the successive straight-chain alkenes from ethylene to pentene. As a result, the potencies of the gases were given as ethylene, 1, propene, 2.25, butene, 4.5 and pentene, 15. It was found that death, when it occurred, resulted from respiratory failure, although it was believed that butene and pentene might have some action on the heart.[51] This latter observation was made more frequently with propene which had been stored for some time than with freshly prepared, uncompressed gas.[52] In some cases, where a mixture of 40 to 50 per cent propene, 20 per cent oxygen and 40 to 30 per cent nitrogen was employed, there was a muscular rigidity which was accompanied by contraction of the oculomotor muscles and resulted in a stare. Electrocardiographic studies on men showed that there was a slowing of the pulse rate during propene anesthesia which returned to normal shortly after the anesthetic was withheld. The lethal dose of propene is said to be about 2/3 more than the anesthetic concentration.[53] The respiratory center of dogs and cats is stated to be stimulated by a narcotic concentration of propene but paralyzed by a lethal one. In cats, dogs and mice, propene seemed to excite some portion of the motor tracts. There was said to be some substance in the propene which was similar in reactions to it, but more powerful pharmacologically.[54]

The results which were obtained by electrocardiographic methods on animals by Riggs and Goulden[55] have been obtained in the same manner for man by Kahn and Riggs.[56] They observed that complete anesthesia occurred on the average after eight inhalations. There was no particular effect on the heart except during complete narcosis. The memory of the patient returned very rapidly after removal of the anesthetic.

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[48] *Cf.* R. M. Waters and E. R. Schmidt, *J. Am. Med. Assoc.*, 1934, **103**, 975.

[49] W. E. Brown, *J. Pharmacol.*, 1924, **23**, 485; *Chem. Abs.*, 1924, **18**, 2921; *Chem. Zentr.*, 1924, **2**, 1955.

[50] L. K. Riggs, *J. Am. Pharm. Assoc.*, 1925, **14**, 380; *Chem. Zentr.*, 1925, **2**, 744; *Chem. Abs.*, 1925, **19**, 3122. See also W. E. Brown and V. E. Henderson, *J. Pharmacol.*, 1926, **27**, 1; *Chem. Abs.*, 1926, **20**, 1869; *Chem. Zentr.*, 1926, **1**, 3082.

[51] For a discussion of the intoxicating effect of ethylene and propene, see B. M. Davidson, *J. Pharmacol.*, 1925, **26**, 27, 33; *Chem. Abs.*, 1925, **19**, 3123; *Chem. Zentr.*, 1926, **1**, 164.

[52] L. K. Riggs and H. D. Goulden, *J. Am. Pharm. Assoc.*, 1927, **16**, 635; *Chem. Abs.*, 1927, **21**, 3980; *Chem. Zentr.*, 1927, **2**, 1864.

[53] J. T. Halsey, C. Reynolds and W. A. Prout, *J. Pharmacol.*, 1926, **26**, 479; *Chem. Zentr.*, 1926, **1**, 3083; *Chem. Abs.*, 1926, **20**, 1869.

[54] The boiling range of the propene used by these workers and prepared by them, was given as: 5 per cent between −50° and −48°C., 50 per cent between −48° and −45°C., 40 per cent between −45° and −40°C., and not more than 5 per cent below −40°C. (i.e., higher boiling). The boiling point of propene has been given as −47.67±0.1°C., and of cyclopropane as −32.89±0.05°C. by A. A. Ashdown, L. Harris and R. T. Armstrong, *J.A.C.S.*, 1936, **58**, 850; *Chem. Abs.*, 1936, **30**, 4823.

[55] L. K. Riggs and H. D. Goulden, *loc. cit.*

[56] M. H. Kahn and L. K. Riggs, *Ann. Intern. Med.*, 1931, **5**, 651; *Chem. Abs.*, 1932, **26**, 1666; *Chem. Zentr.*, 1932, **1**, 1685.

ACETYLENE AS AN ANESTHETIC

In 1923 Gauss and Wieland[57] reported that acetylene from which toxic substances such as phosphine had been removed was an effective anesthetic. The gas was said to have a characteristic, not unpleasant odor and a bitter taste. Using an especially designed machine for the administration, anesthesia was initiated with a mixture containing 60 per cent of acetylene and 40 per cent of oxygen. After 1 minute the hydrocarbon was increased to 70 per cent and then reduced to 60 per cent at the end of another minute. The proportion of acetylene was then diminished until the minimum necessary to maintain anesthesia was reached, usually between 25 and 40 per cent. In 75 per cent of the cases tried, anesthesia was complete after 2 minutes, the duration varying under different requirements between 3 and 136 minutes. There was only occasionally a state of excitement before complete narcosis. No deleterious effects on the body functions were observed. Although recovery was sometimes accompanied by nausea and vomiting for short periods, consciousness returned very shortly after removing the mask.

Rimarski[58] has studied the explosiveness of mixtures of acetylene and air but concluded that there is little danger on this score from its use in anesthesia. He found that, whereas 3.35 per cent was necessary for any explosion, the proportion in most parts of the room was very small and near the patient was only about 1 per cent. The precaution of keeping any hot apparatus or any sources of electric sparks at a distance from the patient was believed to prevent any possibility of a disaster. There appeared to be very little removal of acetylene in breathing, and there was only 1.7 per cent of carbon dioxide in the expired air.

The opposition to acetylene, aside from its inflammability, has been either on the grounds of its odor and irritant action[59] or upon the difficulty of removing acetone vapors from acetylene which has been shipped in a cylinder containing that substance.[60] This latter difficulty has been overcome by Reiber[61] who removed the ketone by passing the gas over an adsorbent such as activated carbon.

According to Heymans and Bouckaert[62] acetylene is less toxic than either chloroform or ether, and it has a different effect on the respiratory center, viz., rather than depressing, it stimulates. A mixture of 80 parts acetylene and 20 of oxygen is said to bring about complete narcosis and muscular relaxation in 2 to 3 minutes. Moreover, acetylene may be used together with nitrous oxide and oxygen, and thus the normal oxygen concentration of the arterial blood is maintained, a desirable effect which cannot be secured when nitrous oxide and oxygen are used alone.

[57] C. J. Gauss and H. Wieland, *Klin. Wochschr.*, 1923, **2**, 113, 158; *Chem. Zentr.*, 1923, **3**, 91; *Chem. Abs.*, 1924, **18**, 1859. See also H. Wieland, British P. 205,240, 1922, to C. H. Boehringer Sohn; *Chem. Abs.*, 1924, **18**, 1180. H. Wieland, U. S. P. 1,526,034, Feb. 10, 1925; *Chem. Abs.*, 1925, **19**, 1757.

[58] W. Rimarski, *Z. angew. Chem.*, 1925, **38**, 409; *Chem. Abs.*, 1925, **19**, 3122. *Münch. med. Wochschr.*, 1925, **72**, 386; *Chem. Zentr.*, 1925, 1, 2389. See also *Z. angew. Chem.*, 1929, **42**, 933; *Chem. Zentr.*, 1929, **2**, 2922.

[59] F. E. Shipway, *Lancet*, 1925, 1, 1126; *Chem. Zentr.*, 1925, **2**, 744; *Chem. Abs.*, 1925, **19**, 3121. For use of fragrant alcohol such as geraniol with acetylene, see H. Wieland, U. S. P. 1,561,130, Nov. 10, 1925; *Chem. Abs.*, 1926, **20**, 95.

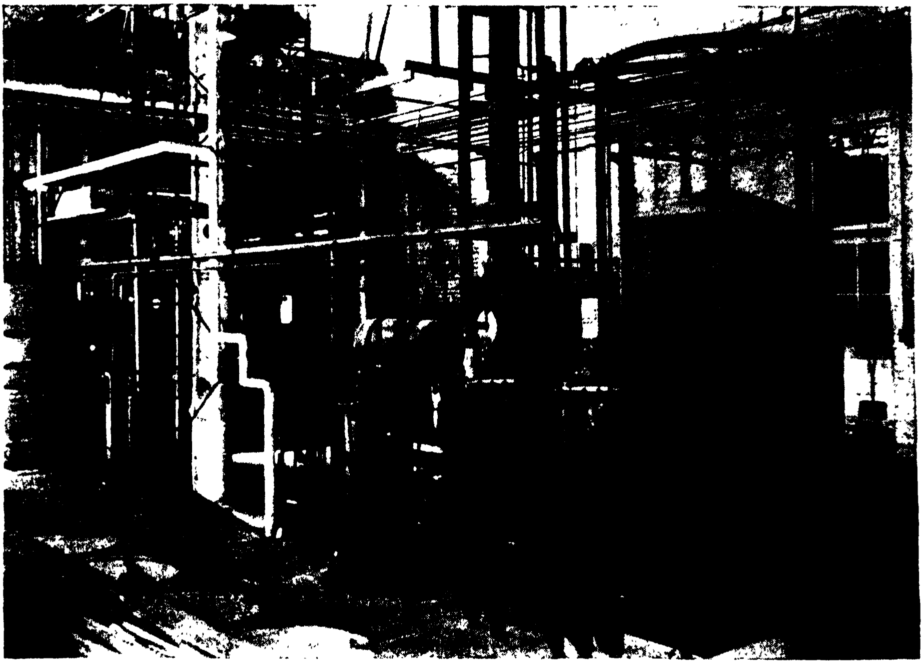
[60] J. Blomfield, *Proc. Roy. Soc. Med.*, 1926, **19**, Sect. Anesthesia, 39; *Chem. Abs.*, 1927, **21**, 961; *Ber. ges. Physiol.*, 1926, **39**, 145; *Chem. Zentr.*, 1927, **2**, 455.

[61] J. Reiber, Austrian P. 114,600, 1929; *Chem. Abs.*, 1930, **24**, 920.

[62] C. Heymans and J. J. Bouckaert, *Compt. rend. soc. biol.*, 1925, **93**, 1036; *Chem. Abs.*, 1926, **20**, 1861; *Chem. Zentr.*, 1926, 1, 1842.

CYCLOPROPANE IN ANESTHESIA

In studying the effect of propene on dogs and cats by means of the electrocardiograph, Caine and Reynolds[63] observed certain cardiac irregularities which disappeared on reducing the concentration of gas and were thought to be caused by some impurity in the gas. These irregularities were not observed in ether, nitrous oxide, ethylene or acetylene. Subsequently, Lucas and Henderson[64] investigated cyclopropane as the possible cause of the irregularities observed by Caine and Reynolds and found not only that this gas was not responsible, but that it was a good anesthetic, from 10 to 12 per cent being sufficient to produce surgical anesthesia in cats.



Courtesy Industrial and Engineering Chemistry

FIG. 313.—Chlorination Unit Employed in **Synthesis** of Cyclopropane. (See Chapter 30) (H. B. Hass, E. T. McBee, G. E. Hinds and E. W. Gluesenkamp)

Cyclopropane has a sweetish odor, like ethylene and chloroform, and is not difficult to breathe.[65] The principal effect observed when it was used on a dog for 1½ hours was a slight drop in blood pressure. Respiratory volume was good, and alkaline reserve and the blood acidity were affected only slightly even on prolonged anesthesia. Cyclohexane was also studied as a possible anesthetic,[66] and was found to cause few or no symptoms of irritation; from these the animals recovered completely. Cyclohexane was 4.8 times as powerful an anesthetic as cyclopropane and 3.2 times as potent for fatal concentrations.

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[63] A. M. Caine and C. Reynolds, *Proc. Soc. Exptl. Med.*, 1926, **23**, 461; *Chem. Abs.*, 1927, **21**, 3958; *Ber. ges. Physiol.*, 1926, **36**, 713; *Chem. Zentr.*, 1926, **2**, 3100.

[64] G. H. W. Lucas and V. E. Henderson, *Can. Med. Assoc. J.*, 1929, **21**, 173; *Chem. Abs.*, 1929, **23**, 4741.

[65] V. E. Henderson and G. H. W. Lucas, *Anesthesia and Analgesia*, 1930, **9**, 1; *Chem. Abs.*, 1930, **24**, 1467; *Chem. Zentr.*, 1930, **2**, 758.

Waters and Schmidt[67] have reported the results of the use of cyclopropane in a large number of cases where anesthesia was desired. Premedication was effected by the hyperdermic injection of from 1/8 to 1/4 grain of morphine (0.008 to 0.016 g.) and from 1/200 to 1/100 grain of scopolamine (0.00032 to 0.00065 g.) about 1½ hours before anesthesia. Anesthesia was carried out using various proportions of cyclopropane up to about 43 per cent, which was the average amount necessary to cause respiratory arrest. It was observed that the oxygen content of the gas must be kept well above 20 per cent. A comparison of the fatalities in regard to time and cause is given in Table 236.

TABLE 236.—*Comparison of Fatalities Resulting After Anesthesia.*

	Extra-Abdominal Cases			Abdominal Cases	
	Ether	Cyclopropane	Ethylene	Ether	Cyclopropane
Number of cases	600	600	600	400	400
Total deaths	23	13	22	27	27
Per cent mortality	3.83	2.16	3.66	6.75	6.75
Time of death					
Day of operation	1	1	1	2	1
1-3 days after operation	4	4	1	5	3
4-7 days after "	1	2	5	8	6
Second week	2	2	4	6	6
Later	15	4	11	6	11
Cause of death					
Pneumonia	5	0	4	6	4
Other respiratory diseases	0	0	1	2	0
Hemorrhage	0	1	0	1	2
Other circulatory diseases	3	5	2	4	4
Toxemia	9	1	9	7	10
Carcinoma	3	4	4	5	4
Shock	0	0	0	1	1
Others	3	2	2	1	2

The results show that there was less tendency toward respiratory troubles when cyclopropane was employed as an anesthetic than when either ethylene or ether was used, but there was a somewhat greater tendency toward circulatory complications. The non-fatal cases are compared graphically as to complications in Figs. 314 and 314A. Cyclopropane does cause some nausea but less emesis (vomiting) than the other anesthetics studied. Pathological changes were found in the heart after necrotomy in some instances, but they could not be conclusively ascribed to the cyclopropane.

Because of the non-irritant properties of this same gas, there was no tendency to laryngospasm, the normal protection from extreme dosage of a gas, and some trouble was experienced in passing gradually between the different degrees of narcosis. The most valuable sign which can be used to indicate the approach of the limit of tolerance is a change in the character of the pulse, such as arrhythmia or an acceleration or deceleration in rate. In fact, Waters[68] has stated that the appearance of extreme irregularities of the heart should be met by a marked reduction in the concentration of cyclopropane in the gas mixture. Seevers, DeFazio and Evans[69] investigated the rate at which cyclopropane and ethylene are absorbed and expelled by the body.[70] They found that the former was more rapid in its activity. The carbon dioxide tension of the tissues was also higher during cyclopropane anesthesia.

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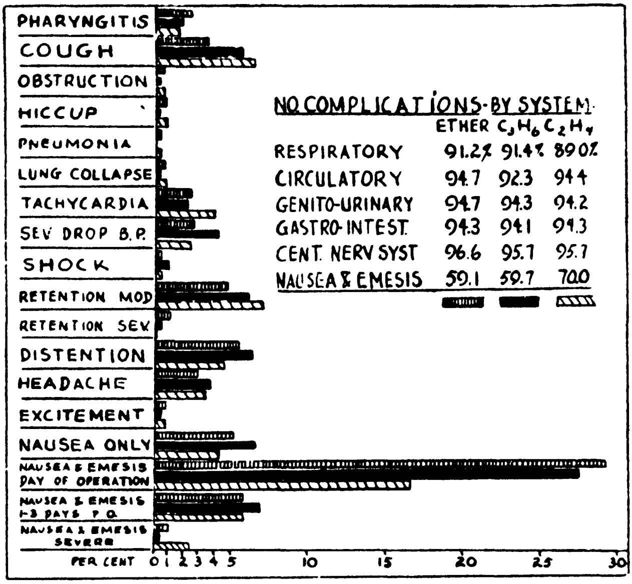
[66] V. E. Henderson and J. E. A. Johnston, *J. Pharmacol.*, 1931, **43**, 89; *Chem. Abs.*, 1932, **26**, 1668; *Brit. Chem. Abs.* **A**, 1931, 1328; *Chem. Zentr.*, 1932, 1, 3199.

[67] R. M. Waters and E. R. Schmidt, *J. Amer. Med. Assoc.*, 1934, **103**, 975. See also F. T. Romberger, *Anesthesia and Analgesia*, 1935, **14**, 65, 136; *Chem. Abs.*, 1935, **29**, 5518. H. R. Griffith, *ibid.*, 253; *Chem. Abs.*, 1936, **30**, 766. L. F. Sise, P. D. Woodbridge and U. H. Eversole, *New Eng. J. Med.*, 1935, **213**, 303; *Chem. Abs.*, 1935, **29**, 7491. G. F. Bradford, *Anesthesia and Analgesia*, 1936, **15**, 256. S. Rowbotham, *Proc. Roy. Soc. Med.*, 1936, **29**, 257. S. Rowbotham, A. Chester, R. Jarmans, G. R. Phillips and T. B. Vaile, *Lancet*, **1935**, **2**, 1110. G. S. Mechling, *J. Oklahoma State Med. Assoc.*, 1935, **28**, 436; *Chem. Abs.*, 1936, **30**, 1125. J. B. Bogan, *Anesthesia and Analgesia*, 1936, **15**, 275. G. S. Mechling and J. A. Moffitt, *J. Oklahoma State Med. Assoc.*, 1936, **29**, 204; *Chem. Abs.*, 1936, **30**, 8396. S. A. Stiles, W. B. Nott, E. A. Rovenstine and R. M. Waters, *Anesthesia and Analgesia*, 1934, **13**, 56. J. A. Moffitt and G. S. Mechling, *ibid.*, 1936, **15**, 225. Preliminary Report of Council on Pharmacy and Chemistry, *J. Am. Med. Assoc.*, 1936, **106**, 292. E. A. Rovenstine and I. B. Taylor, *Am. J. Med. Sci.*, 1936, **191**, 807. F. S. Orcutt and R. M. Waters, *Anesthesia and Analgesia*, 1933, **12**, 45. R. M. Waters, *Brit. Med. J.*, **1936** (2), 1013; *Chem. Abs.*, 1937, **31**, 1095.



NO COMPLICATIONS BY SYSTEM

	ETHER	C_3H_6	C_2H_4
RESPIRATORY	91.2%	91.4%	89.0%
CIRCULATORY	94.7	92.3	94.4
GENITO-URINARY	94.7	94.3	94.2
GASTRO-INTEST.	94.3	94.1	94.3
CENT. NERV SYST	96.6	95.7	95.7
NAUSEA & EMESIS	59.1	59.7	70.0
	▥	■	▨

Courtesy Journal of American Medical Association

FIG. 314.—Post-operative Complications Following Anesthesia with Ether, Cyclopropane and Ethylene in Extra-abdominal Surgery. (R. M. Waters and E. R. Schmidt)

Graph represents percentage incidence of each complication following 600 cases for each anesthetic. Table lists percentage showing no complications.

In anesthetizing a dog the action of cyclopropane is said to lie between ether and ethylene in regard to induction, maintenance and recovery from anesthesia. No immediate untoward effects were observed even after narcosis had been prolonged for a considerable time.[71] Without premedication about 25 per cent cyclopropane was sufficient for anesthesia. This hydrocarbon was found to affect the heart during artificial respiration when administered in considerable amount.

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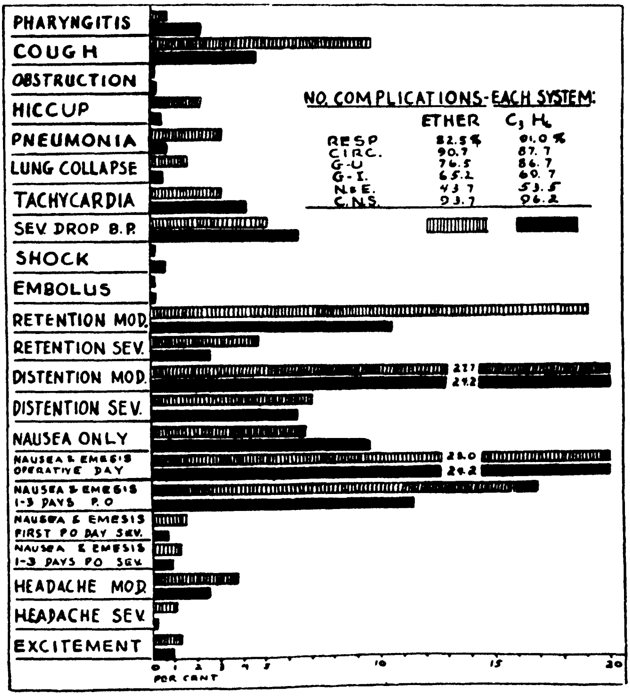
[68] R. M. Waters, *Brit. Med. J.*, **1936**, **2**, 1013.

[69] M. H. Seevers, S. F. DeFazio and S. M. Evans, *J. Pharmacol.*, 1935, **53**, 90; *Chem. Abs.*, 1935, **29**, 2238; *Brit. Chem. Abs.* **A**, 1935, 525.

[70] The solubility of cyclopropane in blood and in water and the determination of this hydrocarbon in these media and in air are discussed by B. H. Robbins, *J. Pharmacol.*, 1936, **58**, 243; *Chem. Abs.*, 1937, **31**, 974.

[71] M. H. Seevers, W. J. Meek, E. A. Rovenstine and J. A. Stiles, *J. Pharmacol.*, 1934, **51**, 1; *Brit. Chem. Abs.* **A**, 1934, 803; *Chem. Abs.*, 1934, **28**, 5136; *Chem. Zentr.*, 1934, **2**, 2859. See also L. F. Shackell and R. E. Blumenthal, *Anesthesia and Analgesia*, 1934, **13**, 133; *Chem. Abs.*, 1935, **29**, 1500; *Chem. Zentr.*, 1934, **2**, 2246.

Because of the quiet breathing of the patient during cyclopropane anesthesia, it has been found a useful agent in thoracic surgery,[72] and it has been employed in obstetrics.[73] Its explosiveness, however, necessitates the use of a special technique. The results obtained in 2200 cases in which cyclopropane was used have been compared by Schmidt and Waters[74] with a like number in which other agents were employed. In these data deaths which resulted from all causes are included as shown in Table 237.



Courtesy Journal of American Medical Association

FIG. 314A.—Post-operative Complications Following Anesthesia with Ether and Cyclopropane in Abdominal Surgery. (R. M. Waters and E. R. Schmidt)

Graph shows percentage incidence of each complication following 400 cases for each anesthetic. Table gives percentage resulting in no complications.

A certain amount of study has been made upon the influence of cyclopropane on the functions of the body. Taylor and Waters[75] found that there is a leucocytosis which occurs after anesthesia whether induced by ether, nitrous oxide, ethylene or cyclopropane. This reaches a maximum about 4 to 8 hours after operation and

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[72] E. A. Rovenstine, *Anesthesia and Analgesia*, 1935, **14**, 257, 270; *Chem. Abs.*, 1936, **30**, 766.

[73] W. Bourie, *Lancet*, 1934, **2**, 20. R. T. Knight, *Anesthesia and Analgesia*, 1936, **15**, 63. H. R. Griffith, *Can. Med. J.*, 1934, **31**, 157.

[74] E. R. Schmidt and R. M. Waters, *Anesthesia and Analgesia*, 1935, **14**, 1; *Chem. Abs.*, 1935, **29**, 3401.

[75] I. B. Taylor and R. M. Waters, *Anesthesia and Analgesia*, 1935, **14**, 276; *Chem. Abs.*, 1936, **30**, 766.

TABLE 237.—*Post-operative Deaths in 4400 Clinical Inhalation Anesthesias.*

	Cyclopropane	Other Agents
Cases	2200	2200
Total deaths	94	87
Mortality per cent	4.19%[a]	3.99%
Time of Death:		
Day of operation	0	2
1st day P.O.	6	6
2nd–3rd day P.O.	20	12
4th–7th day P.O.	11	22
2nd week	18	14
Later	39	31
Cause of Death:		
Pneumonia	5	14
Other respiratory	3	6
Hemorrhage	7	2
Other circulatory	14	9
Toxemia	32	22
Carcinoma	17	15
Shock	3	2
Anesthesis	1	2
Others	12	15

[a] Includes late deaths, malignancy, etc.

continues for 2 or 3 days. Robbins[76] has observed that anesthetics such as ethylene and cyclopropane cause a cessation of salivary flow by depressing the secretory center.

Peoples and Phatak[77] have investigated the effect of cyclopropane on rabbit's intestine suspended in Locke's solution.[78] A mixture of the hydrocarbon and oxygen such as would be used in anesthesia (10 to 25 per cent cyclopropane) is bubbled through the solution. In the cases observed there was an increase in the tone of the muscles of the intestine and decrease in the amplitude of contraction. The stimulation was proportional to the concentration and reached a maximum for 25 per cent cyclopropane. From these results, Peoples and Phatak believed that there should be less tendency toward post-operative intestinal stasis and the resulting distension when cyclopropane is used as an anesthetic. In this connection Waters[79] states that work of Meek on dogs has shown that deep cyclopropane anesthesia either averts or inhibits both contraction and propulsion phenomena of the intestine. Prompt return to normal, or greater than normal (6 out of 14 cases) occurred after removal of the wash.

The effect of cyclopropane on the heart and circulatory system has been intimated previously. Waters[80] has found that intravenous injection of epinephrine in a dog under light chloroform anesthesia will frequently precipitate ventricular fibrillations[81] but does not do so under light cyclopropane anesthesia.

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[76] B. H. Robbins, *J. Pharmacol.*, 1935, **54**, 426; *Chem. Zentr.*, 1936, 1, 2972; *Chem. Abs.*, 1936, **30**, 1142.

[77] S. A. Peoples and N. M. Phatak. *Proc. Soc. Exptl. Biol. Med.*, 1935, **33**, 287; *Chem. Abs.*, 1936, **30**, 6813; *Chem. Zentr.*, 1936, 1, 2586.

[78] This is a solution containing 0.9 per cent sodium chloride, 0.024 per cent calcium chloride, 0.042 per cent potassium chloride, from 0.01 to 0.03 per cent sodium bicarbonate and 0.1 per cent dextrose. The latter is not essential. This solution is maintained in an atmosphere of oxygen, and it is said to be possible to keep mammalian hearts working in this solution for some time.

[79] R. M. Waters, *Brit. Med. J.*, **1936**, **2**, 1013.

[80] R. M. Waters, *loc. cit.*

[81] Ventricular fibrillations are the independent, as opposed to co-ordinated, contractions of the muscle fibres of the ventricles. The result is usually fatal, and is said not to have been observed electrocardiographically in man for this reason.

Chapter 54

Thermodynamics and Its Application to Petroleum Technology

The application of thermodynamic principles to the field of petroleum technology has been made possible through the innumerable investigations of a vast number of contributors. Although LeChatelier[1] had pointed out the importance of a knowledge of chemical equilibria in industrial chemistry as early as 1888, for over a period of approximately 35 years relatively little work was conducted along the lines of research in this field. Perhaps the former widespread prejudice against any practical use of chemical thermodynamics was not without foundation, as Lewis and Randall[2] have stated in their critical review of this science. The correlation of the exact laws of thermodynamics with poorly founded or even erroneous assumptions cannot be expected to give representative predictions. In addition, there was a further disadvantage, especially in the organic field, in the almost total lack of adequate accurate thermal data. Determinations along these lines since about 1925 have, however, furnished a basis for the introduction of this science into the widespread field of the petroleum industry.

The value of numerous thermodynamic concepts, such as enthalpy, entropy, fugacity and free energy, is rapidly becoming recognized not only in scientific investigations but also in commercial enterprises. For these reasons a general discussion of such topics, especially in regard to their practical application, has been incorporated in this chapter. However, it should be stressed that in many instances the values given are by no means absolute or final. Subsequent revision of these quantities may be expected as a direct result of refinements in experimental technique, elimination of observational errors and recalculations in view of later and more exact fundamental data. Yet variations of this type have not been uncommon in the other fields of chemistry of longer standing, and so these changes may be expected to occur in an analogous manner. The free energy values are typical examples of data falling into this class. However, the reasons for these deviations will be considered and explained in the following pages.

CHEMICAL THERMODYNAMICS

The work of Lewis and Randall[3] contributed largely to the establishment of thermodynamics in general chemistry. However, their study was devoted almost exclusively to inorganic chemistry as the prerequisite organic data were almost entirely lacking at that time (1923). The systematic researches of Parks and his collaborators, together with the observations of numerous other investigators, greatly enhanced the literature pertaining to the field of organic compounds. In 1932, the latter efforts were culminated, critically evaluated and embodied into a concise volume by Parks and Huffman.[4] Over 300 free energy values representing hydrocarbons, alcohols, phenols, acids, halides and organic compounds of oxygen, sulphur and nitrogen were included in this text. These results, according to Parks,[5] although merely preliminary and semi-quantitative, serve as an initial foundation for "thermodynamic organic chemistry." "Moreover, at the present time," Parks continues, "new free energies and more accurate ones are being added to the literature at an accelerated pace."

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[1] H. LeChatelier, *Ann. mines*, 1888, (8) 13, 157.

[2] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York and London, 1923.

[3] G. N. Lewis and M. Randall, *loc. cit.*

Before discussing free energy and the application of this quantity to industrial problems, it is necessary to review a few of the relations and definitions involved.[6]

The Concept of Free Energy

Although free energy may be expressed quite simply in a mathematical sense (as will be shown shortly), this concept does not lend itself to a thorough verbal description. A rigorous derivation, such as that of Gibbs[7] and others, derived from a scientific and mathematical basis, is tedious and involved. However, Francis and Kleinschmidt[8] have employed a simple analogy which may help to explain the meaning of free energy.

These authorities consider as an example the flow of water in a system composed of two reservoirs, *A* and *B*, joined by a pipe. By measuring the height of the water levels in both *A* and *B* from some arbitrary datum plane (or in other words, the "head" or "gravitational potential"), the respective tendency of the water to flow from one to the other can be ascertained. In addition, it will be noted that the difference between the heights of the water levels in the two reservoirs is a measure of the work that could be done, theoretically, in allowing a given mass of water to flow through a turbine or other device in going from the higher reservoir to the lower. From this example, Francis and Kleinschmidt define "gravitational potential" either as the tendency of the material (that is, the water) to change its position, or as the available work that could be performed by allowing a unit quantity of material to change its position. Gibbs and others have shown that there exists a property of matter which bears essentially the same relation to chemical change that the "head" or "gravitational potential" has to the flow of water. In the nomenclature of Gibbs, this property is known as the "thermodynamic potential," in a sense analogous to that used above for the gravitational potential. Lewis[9] prefers to refer to this quantity as "free energy." "Available energy" is another synonym that has been suggested. However, of the three terms, Lewis' "free energy" is the one that has become most generally accepted.

Thus, from the above discussion, it will be seen that the change in free energy may be regarded as the driving force of a reaction, or the high-grade energy that would be made available during the transformation. Briefly then, if a large quantity of high-grade energy is liberated during a change, the reaction is thermodynamically possible and spontaneous. If, however, the transformation involves the passage from a state of lower to higher free energy levels, the latter can only be accomplished by the addition of energy, as, for instance, mechanically (by compression), electrically (by electrolysis or ionization) or thermally, just as in the case of the water analogy, where in order to increase the gravitational potential it is necessary to use a pump.

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[4] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, **1932**.

[5] G. S. Parks, *Chem. Rev.*, 1936, **18**, 325; *Chem. Abs.*, 1936, **30**, 5113.

[6] A thorough discourse on thermodynamics cannot be included in this text. Reference should be made to G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York and London, **1923**. H. S. Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York (Second Edition), **1930**, Chapter 2. Also J. H. Perry, "Chemical Engineers' Handbook," McGraw-Hill Book Co., Inc., New York and London, **1934**, Chapter 5.

[7] In this connection, see W. R. Longley and R. G. Van Name, "The Collected Works of J. Willard Gibbs," Longmans, Green and Co., New York, 1928, **1**, **87**.

[8] A. W. Francis and R. V. Kleinschmidt, *Oil and Gas J.*, 1929, **28** (29), 118; *Chem. Abs.*, 1930, **24**, 2369.

[9] G. N. Lewis and M. Randall, *loc. cit.*

However, for the actual occurrence of a reaction to an appreciable extent, the fulfillment of the free energy requirements is a necessary but not a sufficient condition. Rates of reaction must also be considered in answering this question. Francis and Kleinschmidt[10] carry their water analogy one step further, and compare the pipe line joining the reservoirs to a catalyst for a chemical reaction. When the main connecting the two bodies is large, the rate at which the water flows from the higher to the lower level is quite rapid, and conversely, when the pipe is small, the rate will be slower. Thus, the pipes with their different rates of flow may be regarded as catalysts, since the latter have the property of affecting the speed of chemical transformations. It should be borne in mind, however, that no pipe exists which can cause the water to flow from a lower to a higher level without the application of external work. The same principle is true of catalysts, namely: A reaction that is thermodynamically unfeasible (i.e., one in which the free energy change is from a lower to a higher level) cannot be forced to proceed by means of catalysts. In this respect, Francis and Kleinschmidt point out the dual role played by temperature. The addition of energy, in the form of heat, directly affects the free energy (as will be shown later in this chapter), so that reaction which might be impossible thermodynamically at one temperature may become possible at another. Furthermore, high temperatures tend to break down chemical inertness or resistance to change, and allow changes to proceed at greater speeds.

THERMODYNAMIC NOMENCLATURE

Since free energy calculations are used primarily in scientific rather than technical operations, it is customary to employ the metric rather than the British system of units. The thermodynamic variables in most general application, together with their symbols and units, are listed below:

	Symbol	Units
Volume	V	Liters
Temperature (absolute)	T	°K. (°K. = °C. + 273.1)
Pressure	P	Atmospheres
Heat (general)	q	Cal.
Heat capacity	C	Cal./°K./g. (or mole)
Heat content	H	Cal.
Internal energy	U	Cal.
Entropy	S	Cal./°K.
Free energy	F	Cal.
Work content	A	Cal.

Of the variables given above, temperature, pressure and heat capacity are termed "intensive properties," that is, they are independent of the quantity of material.[11] The others included are "extensive" and are proportional to the mass of the substance involved. However, it is convenient to compare these functions on a molar basis, for instance, volume per mole and entropy per mole, so that in this case molal entropy[12] or molal volume are intensive quantities, that is, are independent of the amount of material taken.

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[10] A. W. Francis and R. V. Kleinschmidt, *loc. cit.*

[11] Consult G. N. Lewis and M. Randall (*loc. cit.*) for a discussion of intensive and extensive properties.

[12] Molal entropy is generally measured in terms of "entropy units" (abbreviated as E.U.) and has the dimensions of calories per degree absolute per mole.

As to the general meaning of the above-mentioned terms, volume, temperature and pressure are in common use and require no further explanation. The symbol q is used to designate any quantity of heat, in general. H represents the heat content of a system, while U is the internal energy, or the actual energy content of the material under consideration. These quantities are related thermodynamically by the equation

$$H = U + PV$$

Similarly, F, the free energy or chemical potential and A, the work content, can be expressed as

$$F = A + PV$$

(The significance of these terms will be seen more clearly in the discussion given in the following section.) The entropy, S, is a quantity, which like free energy does not permit a rigorous verbal description, but it will suffice to say it is a measure of the waste thermal energy in a system. For a reversible process, an infinitesimal increase in entropy is related to the general heat term, q, by the differential equation:

$$dS = \frac{dq}{T}$$

where dq represents an infinitesimal amount of heat absorbed. A finite change in entropy, designated by ΔS, is given by

$$\Delta S = \frac{q}{T}$$

The heat capacity, C, is a very useful function and is governed by the differential equation

$$C = \frac{dq}{dT}$$

where dq and dT represent infinitesimal increments in the heat quantity and absolute temperature, respectively. The heat capacity is generally designated as C_p for a system maintained at constant pressure or C_v for one maintained at constant volume. Mathematically, the latter quantities are:

$$C_p = \left[\frac{\delta H}{\delta T}\right]_p$$

$$C_v = \left[\frac{\delta U}{\delta T}\right]_v$$

which, stated in words, are: The heat capacity at constant pressure is equal to the rate of change of the heat function with respect to temperature at constant pressure, and the heat capacity at constant volume is equal to the rate of change of internal energy with respect to temperature at constant volume. The heat capacity is also related to the change in entropy

$$\frac{dS}{dT} = \frac{C}{T}$$

or

$$dS = C\, d\ln T$$

These relations are only a few of the many possible thermodynamic equations. There are several that require a more detailed consideration, and, therefore, the more important of these will now be discussed.

Relationship between Change in Heat Content and Change in Free Energy

The change in heat content (ΔH) and the change in free energy (ΔF) are in almost constant use in thermodynamic calculations. Although in a few instances these two quantities may be very nearly equal numerically, this is by no means the general case. The differentiation between these two quantities has been discussed by Parks and Huffman[13] and will be shown below.

Consider a simple system (such as a group of reacting molecules) which may be represented in its initial state by the subscript A, undergoing a transposition to some reproducible state B. Furthermore, suppose that this transformation occurs at constant temperature and pressure and in such a manner that no work is involved except that which is necessary to maintain the conditions of constant pressure. The increase in a thermodynamic variable (such as heat content, free energy, volume and so forth, represented by the general symbol X) will be given by:[14]

$$\Delta X = X_B - X_A \quad \text{or} \quad -\Delta X = X_A - X_B$$

In the case of the heat content, H (or heat function, as it is sometimes called), $\Delta H = H_B - H_A$ and is the heat absorbed by the system under these conditions. Likewise, $-\Delta H$ will represent heat evolved. From the first law of thermodynamics, ΔH is related to the increase in internal energy,[15] ΔU, and the change in the pressure-volume product, $\Delta(PV)$, by the relation:

$$\Delta H = \Delta U + \Delta(PV)$$

Since this reaction was assumed to take place at constant pressure,

$$\Delta H = \Delta U + P\Delta V$$

If the change in volume is positive (i.e., V_B is greater than V_A), the $P\Delta V$ term represents the work done by the system on the surroundings. On the other hand, if the transformation is accompanied by a decrease in volume, the above term is a measure of the work done upon the system by the surroundings. In either case the work involved is not considered available for useful purposes.

Although the change in the intrinsic energy, ΔU, is of a more fundamental nature than the change in heat content, the latter quantity is of more practical importance to the chemist since most processes take place at constant pressure. Thus, if heat is evolved in the above transformation, there will be a decrease in the heat content, and the heat evolved ($-\Delta H$) is the heat of reaction, as determined in a constant-pressure calorimeter. In other words, $-\Delta H$ is symbolic of the useful energy (measured as heat) available in a reaction carried out at constant pressure and temperature.

The maximum work ($-\Delta A$) obtainable from the system is another thermodynamic variable. Under the assumed condition of constant pressure, however, $-\Delta A$ does not represent the actual work available for useful purposes, since as mentioned previously, a certain amount of work, $P\Delta V$, is usually necessary to maintain the conditions of constant pressure. Subtracting the latter from the value of the maximum work, the decrease in free energy is obtained:

$$-\Delta F = -\Delta A = P\Delta V$$

---

[13] G. S. Parks and H. M. Huffman, *loc. cit.*

[14] Using the calculus notation, a finite change in a thermodynamic variable, such as X, is usually designated as ΔX (the difference between the values of that quantity in the final and initial states). Similarly, dX represents an infinitesimal increment. It should be noted that these changes may be either positive or negative.

[15] This quantity is also known as the energy content, or intrinsic energy. G. N. Lewis and M. Randall (*loc. cit.*) use the symbol ΔE to represent this variable.

It will be seen, therefore, that $-\Delta F$ represents the maximum amount of useful work that can be obtained from a reaction occurring at constant temperature and pressure.[16]

The free energy is related to the heat content and entropy[17] by the fundamental thermodynamic equation:

$$F = H - TS$$

or for an isothermal process conducted at constant pressure,

$$\Delta F = \Delta H - T\Delta S$$

where T is the absolute temperature, S is the entropy, and ΔS is the increase in entropy in the system and is the difference between the entropy value for the product and that associated with the reactants. (ΔS is a measure of the degree of irreversibility of a reaction or degradation of the system as a whole.) Parks and Huffman suggest transposing the latter equation to give:

$$-\Delta H = -\Delta F - T\Delta S$$

Here the term $-\Delta H$ represents the total decrease in useful energy during the process, $-\Delta F$ is the decrease in useful energy convertible to work and $-T\Delta S$ is the decrease in unavailable energy (heat that cannot be converted into useful work[18] at constant temperature and pressure).

THE SIGNIFICANCE OF ΔF

The importance of the change in free energy in determining the direction of a chemical reaction has been stressed by Parks and Huffman. Thus, in the previous case, assuming a reaction to take place at constant temperature and pressure, if ΔF has a large negative value, the transformation may occur spontaneously. If ΔF is positive (indicating a positive increment in the variation of free energy), reaction will proceed to an appreciable extent only through the application of external work or energy. On the other hand, when $\Delta F = 0$, a state of equilibrium exists, and no further change is to be expected.

In the case of the formation of one mole of water from its elements at 25°C. and one atmosphere pressure, the change in free energy is given by the reaction:

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} = H_2O_{(l)};\ \Delta F^{\circ}_{298} = -56{,}560 \text{ cal.}$$

In actuality, after this reaction is once initiated, it proceeds quite vigorously to completion. The reverse of the above equation, i.e., the decomposition of water into its elements at 25°C. can only be accomplished by a process such as electrolysis. Transformations involving a change of state, such as the conversion of ice to water at 0°C. or water to steam at 100°C. and atmospheric pressure, are examples of equilibrium reactions and are accompanied by no change in ΔF at the respective temperatures.

Since the free energy change indicates the degree of completion of a reaction, by means of the thermodynamic relationship,

$$\Delta F^{\circ}_{T} = -RT \ln K$$

---

[16] It will be noted that H bears the same relation to U as F bears to A. Thus, $H = U + PV$ and $F = A + PV$ However, since most reactions are carried out at constant pressure rather than at constant volume, C_p, H and F are in much more general use than the corresponding C_v, U and A.

[17] The entropy may be considered as a measure of the waste thermal energy, that is, energy not available for conversion into mechanical work.

[18] The term "useful work" as used here does not include work expended in maintaining the system at constant pressure.

where R is the gas constant, T is the absolute temperature (°K), it is possible to obtain the equilibrium constant, K, for the reaction. Furthermore, from the latter value it is possible to calculate the actual equilibrium pressures or concentrations which should be present in the system under equilibrium conditions.

It should be noted, however, that whereas ΔF is indicative of the direction and extent of a chemical reaction, yet no information as to the time necessary to reach this state of equilibrium may be obtained from these data. Parks and Huffman discuss this serious limitation of thermodynamics. Thus, in the case of the formation of liquid water from its elements at 25°C., in the absence of a catalyst or a starting mechanism (such as an electric spark), the reaction velocity is extremely slow due to the low reactivity of the substances involved. However, as the above authorities state, this property of chemical inertness, although frequently a serious handicap, is oftentimes a decided advantage. For instance, it makes possible the existence of many compounds (such as benzene) which from the viewpoint of thermodynamics are unstable with respect to decomposition to their constituent elements.

EVALUATION OF ΔF

Unfortunately, there is no manner in which ΔF can be measured directly, as for instance, can be done with heats of combustion and heats of reaction. However, the free energy change in a reaction can be readily calculated from experimental data. In general, four methods are available, namely:

(1) From equilibrium data and measurements of the equilibrium constant, according to the relation

$$\Delta F^{\circ}_{T} = -RT \ln K$$

(2) From data obtained with an electric cell, involving the reaction in question. By measurement of the reversible electromotive force, E, the increase in free energy may be obtained from the formula

$$\Delta F = -N\mathbf{F}E$$

where N is the number of chemical equivalents involved in the transformation and **F** is Faraday's equivalent.[19]

(3) From the fundamental thermodynamic equation defining free energy, discussed previously,

$$\Delta F = \Delta H - T\Delta S$$

(4) From a combination of chemical reactions, for which the corresponding free energy values are known, to give the desired reaction.

However, each of these are subject to definite restrictions and inherent errors, due to many factors.

The first method may be used when the necessary equilibrium data are available at one or more temperatures.[20] However, Parks[21] has stated that such studies are naturally limited to interactions which are not unduly complicated by side reactions. Furthermore, the quantities of reactants and products existing under equilibrium conditions must be sufficiently large to measure without introducing appreciable errors. However, with moderate accuracy in the determination of K, the free energy values are usually quite satisfactory, a 10 per cent error in the equilibrium constant at 500°K. (227°C.) involving an error of only 90 cal. in ΔF°_{500}, according to Parks and Huffman.[22] Parks points out the fact that by the use of specific catalysts and improvements in analytical technique, this method may eventually become more extensive in applicability.

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[19] The values usually employed for this constant are: **F** = 96,500 coulombs per equivalent or 23,068 cal. per volt equivalent.

[20] For example, see R. N. Pease and E. S. Durgan (*J.A.C.S.*, 1928, **50**, 2715; *Chem. Abs.*, 1928, **22**, 4459; *Brit. Chem. Abs.* **A**, 1928, 1324) and F. E. Frey and W. F. Huppke (*Ind. Eng. Chem.*, 1933, **25**, 54; *Brit. Chem. Abs.* **A**, 1933, 227; *Chem. Abs.*, 1933, **27**, 654). Also G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, 1932.

[21] G. S. Parks, *Ind. Eng. Chem.*, 1933, **25**, 887; *Chem. Abs.*, 1933, **27**, 4473; *Brit. Chem. Abs.* **A**, 1933, 1014.

The electromotive force measurement method permits a very accurate estimation of free energy values. Unfortunately, its usefulness with respect to organic reactions is almost completely confined to certain simple oxidation-reduction mechanisms.[23]

The use of the third method, which is the most general one, involves an application of the third law of thermodynamics.[24] In order to obtain ΔS, however, an extensive knowledge of thermal data is required. Such data were almost completely lacking prior to about 1925. From low-temperature specific heat observations, the entropy may be calculated quite readily. In some cases, ΔH can be obtained by direct measurement of the heat of reaction by usual calorimetric procedures. Usually, this quantity must be evaluated indirectly from heats of combustion of the various substances involved by the application of Hess' law.[25] The use of such data may lead to a considerable error, since the major portion of the available combustion data was obtained in the early thermochemical studies and is subject to some uncertainty.[26] Much later determinations[27] on heats of combustion are providing more reliable values. However, Parks and Huffman have stated that although that procedure is the simplest and most convenient method, in most cases it cannot yield satisfactory results with respect to free energy values until the heat of combustion of the compounds involved are measured to within 0.02 or 0.03 per cent. According to these authorities, this accuracy is by no means impossible with the calorific facilities now available and with reasonable technique.

The fourth method involves the combination of various chemical equations and their corresponding free energies to give the desired reaction and its free energy value, as indicated by the equation:

$$A + B = C;\ \Delta F^\circ = \Delta F_C^\circ - (\Delta F_A^\circ + \Delta F_B^\circ)$$

where ΔF° is the free energy of reaction, and ΔF_A°, ΔF_B° and ΔF_C° represent the free energies of formation of substances *A*, *B* and *C*, respectively. Of course, the accuracy of the result in this case is directly dependent upon the accuracy of the other free energy values, since the errors involved are directly accumulative.

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[22] G. S. Parks and H. M. Huffman, *loc. cit.*

[23] One of the present applications is the conversion of hydroquinone to quinone, as investigated by J. B. Conant and L. F. Fieser, *J.A.C.S.*, 1923, **45**, 2194; *Chem. Abs.*, 1923, **17**, 3866; *J.C.S.*, 1923, **124** (2), 727 and E. Schreiner, *Z. physik. Chem.*, 1925, **117**, 57; *J.C.S.*, 1925, **128** (2), 978; *Chem. Abs.*, 1926, **20**, 6. See also G. S. Parks and H. M. Huffman, *loc. cit.*

[24] According to G. N. Lewis and G. E. Gibson, *J.A.C.S.*, 1920, **42**, 1528; *Chem. Abs.*, 1920, **14**, 2880; *J.C.S.*, 1920, **118** (2), 585: "If the entropy of each element in some crystalline form be taken as zero at the absolute zero, the entropy of any pure crystal at the absolute zero is zero, and the entropy of any other substance is greater than zero." Most authorities agree that this is the most satisfactory statement of the third law of thermodynamics. See E. D. Eastman, *Chem. Rev.*, 1936, **18**, 257; *Chem. Abs.*, 1936, **30**, 5112, for a discussion of the third law.

[25] See A. L. Marshall, "Thermochemistry," in H. S. Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York, **1930**, 285.

[26] In this connection it should be noted that G. S. Parks and H. M. Huffman (*loc. cit.*) have stated that many of the combustion values as given in the International Critical Tables (McGraw-Hill Book Co., Inc., 1929, **5**, 162) are in error from 1000 to even over 3000 cal. Although this represents, in general, a percentage error of about 0.1 per cent in the heat of combustion value, it has a much more appreciable effect on the heat of reaction and consequently the free energy, due to the loss of significant figures by subtraction.

[27] In this respect, consult F. D. Rossini, *Bur. Standards J. Research*, 1931, **6**, 37; 1932, **8**, 119; 1934, **13**, 21; *Chem. Abs.*, 1931, **25**, 1727; 1932, **26**, 2109; 1934, **28**, 6065; *Brit. Chem. Abs.* **A**, 1931, 433; 1932, 341; 1934, 1071. G. B. Kistiakowsky, H. Romeyn, Jr., J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J.A.C.S.*, 1935, **57**, 65; *Brit. Chem. Abs.* **A**, 1935, 304; *J. Inst. Pet. Tech.*, 1935, **21**, 89A; *Chem. Abs.*, 1935, **29**, 2065. G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J.A.C.S.*, 1935, **57**, 876; *Chem. Abs.*, 1935, **29**, 4254; *Brit. Chem. Abs.* **A**, 1936, 825; *J. Inst. Pet. Tech.*, 1935, **21**, 255A. See also W. A. Roth et al. in H. Landolt and R. Börnstein, "Physikalisch-chemische Tabellen," 5th Edition, revised by W. A. Roth and K. Scheel, J. Springer, Berlin, **1931**.

FREE ENERGY OF FORMATION

From a table of free energies of formation for various substances, the increase in free energy in a reaction may be calculated, as indicated in method (4) given above. However, since the numerical value of these quantities varies considerably with the temperature, it is necessary to establish certain definite conditions in order that they may be comparable. For these reasons, each element is taken in a standard reference state[28] which usually is its most stable form at room temperature and 1 atmosphere pressure.[29]

In accordance with these conditions, the free energy of formation of a compound is the change in the free energy value when one mole of the substance is formed isothermally in its standard state at 1 atmosphere pressure from its constituent elements. As a matter of convenience, these values, commonly called "free energies," are usually calculated at 25°C. (298.1°K.) and are designated as ΔF°_{298}. The free energies of the various elements in their respective standard states are arbitrarily taken as zero.

According to Parks and Huffman[30] there are relatively few instances in which the first method given previously for the determination of free energy (involving the equilibrium constant) may be used. One exception to this is the synthesis of methane from carbon and hydrogen at 1400°K. (1127°C.). By means of catalysts such as nickel, cobalt, iron or platinum this reaction may be carried out at 600°K. (327°C.).[31] However, due to inaccuracies in thermal data, especially high-temperature specific heats, and difficulties in determining the equilibrium constant, extrapolation of the free energy values obtained at the high temperatures to 25°C. may introduce serious errors. Therefore, the only other available method, that involving the third law, is generally employed for evaluating the free energy of hydrocarbons.

The standard free energy of formation is represented by

$$\Delta F^\circ_{298} = \Delta H^\circ_{298} - T\Delta S^\circ_{298}$$

where ΔH°_{298} is the heat of formation (change in heat content for the process of formation), ΔS°_{298} is the increase in entropy (the difference between the absolute entropy of the hydrocarbon and that associated with the requisite number of atoms of carbon and hydrogen) and *T* is the absolute temperature (298.1°K.). The heat of formation may be obtained from tables or calculated from heats of combustion values. The increase in entropy, however, must be calculated from molal entropies, which may be evaluated from low-temperature instantaneous heat capacities and thermal data pertaining to changes of state, using the method introduced by Nernst.[32] Thus, if the entropy at 0°K. (— 273.1°C.), S_O, may be taken as zero for a pure, perfectly crystalline substance, then the molal entropy at 25°C. is given by:

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[28] The standard states are gas, liquid and solid, and are indicated by the subscripts (g), (l) and (s), respectively. In any reaction, it is important that the states be given, as, for example, thermodynamically butane may be considered in the standard state as a liquid (for comparative purposes), although in reality under the conditions chosen to designate the standard state (25°C. and 1 atmosphere) this is impossible. Thus, the standard state of carbon is taken as β-graphite, whereas sulphur is considered to be in the rhombic form under these conditions. Hydrogen, nitrogen and oxygen are referred to as diatomic gases (H_2, N_2 and O_2, respectively).

[29] The symbol X° refers to any thermodynamic quantity corresponding to a standard state. Thus, ΔH° is the "standard change in heat content." However, it is customary to denote the absolute temperature at which this quantity is determined by a subscript. As an example, the standard heat of formation of a compound at 25°C. (298.1°K.) is ΔH°_{298}, whereas at 150°C. (423.1°K.) it would be expressed as ΔH°_{423} and, in general, at T°K., as ΔH°_T.

[30] G. S. Parks and H. M. Huffman, *loc. cit.*

[31] See Carleton Ellis, "The Chemistry of Petroleum Derivatives." The Chemical Catalog Co., Inc., New York, 1934, 105.

$$S_{298} = \int_{T=0}^{T=298} \frac{dq}{T}$$

where dq is an infinitesimal amount of heat absorbed.[33] This method has been applied to over 120 organic compounds by Parks and his collaborators.[34]

The free energy values of the hydrocarbons have been investigated more thoroughly than those of any other class of organic compounds. One reason for this is that the former substances naturally fall into homologous series in which not only the usual physical properties but also certain thermodynamic properties show regularities that are quite pronounced.

Normal Paraffins. In Table 238 are listed the standard free energies of formation of 8 normal paraffins from their elements at 298.1°K. (25°C.) and 1 atmosphere pressure. Also included in this table are the molal entropy, the heat of formation and the standard entropy of formation for each substance at this temperature. In the final column is tabulated the maximum fortuitous error (due to inaccuracies in the values of heats of combustion and entropies) as given by Parks.[35] Although these uncertainties may appear quite large, Parks has stated

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[32] W. Nernst, *Ann. Physik,* 1911, (4) **36**, 395; *Chem. Zentr.*, 1911, **2**, 1718; *Chem. Abs.*, 1912, **6**, 175; *J.C.S.*, 1911, **100** (2), 964. An aneroid calorimeter with liquid air as heat absorbing agent is used to determine specific heats and latent heats of fusion and vaporization down to about 90°K. (—183°C.). See G. E. Gibson, W. M. Latimer and G. S. Parks, *J.A.C.S.*, 1920, **42**, 1533; *Chem. Abs.*, 1920, **14**, 2880; *J.C.S.*, 1920, **118** (2), 585 and G. S. Parks, *J.A.C.S.*, 1925, **47**, 338; *J.C.S.*, 1925, **128** (2), 491; *Chem. Abs*., 1925, **19**, 1085, for a discussion of the methods employed. See also *Bur. Standards Sci. Paper,* **197** (1913) for the procedure in making the determinations and calculating the heat capacities. In order to obtain entropy values for the range O°K. to 90°K. (—273 to —183°C.) the extrapolation formula of K. K. Kelley, G. S. Parks and H. M. Huffman, *J. Phys. Chem.*, 1929, **33**, 1082; *Brit. Chem. Abs.* **A**, 1930, 24; *Chem. Abs.* 1930, **24**, 775, is used. A synopsis of this method has also been given by G. S. Parks and H. M. Huffman. "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, **1932**, 240.

[33] In the case of liquids, Parks and Huffman use the expression:

$$S_{298} = \int_{0}^{90} \frac{C_{p(\text{crystals})}}{T}\,dT + \int_{90}^{T_M} \frac{C_{p(\text{crystals})}}{T}\,dT + \frac{\Delta H_{\text{fusion}}}{T_M} + \int_{T_M}^{298.1} \frac{C_{p(\text{liquid})}}{T}\,dT$$

where T_M is the melting point of the solid phase and ΔH is the heat of fusion. (All values are per mole.) The first of these integrals is evaluated by the method of K. K. Kelley, G. S. Parks and H. M. Huffman, *loc. cit.* The remaining integrals are most readily determined by graphical integration. In the case in which the standard state of the substance under investigation is gaseous, it is necessary to add two more terms involving the heat of vaporization and the specific heat of the vapor in a manner analogous to that given above. See G. S. Parks and H. M. Huffman, *loc. cit.*, for examples illustrating this general method.

[34] This series of investigations consists of the following: G. S. Parks, *J.A.C.S.*, 1925, **47**, 338; *Chem. Abs.*, 1925, **19**, 1085; *J.C.S.*, 1925, **128** (2), 764. G. S. Parks and K. K. Kelley, *J.A.C.S.*, 1925, **47**, 2089; *Chem. Abs.*, 1925, **19**, 2903; *J.C.S.*, 1925, **128** (2), 949. G. S. Parks and C. T. Anderson, *J.A.C.S.*, 1926, **48**, 1506; *Brit. Chem. Abs.* **A**, 1926, 784; *Chem. Abs.*, 1926, **20**, 2444. G. S. Parks and H. M. Huffman, *J.A.C.S.*, 1926, **48**, 2788; *Chem. Abs.*, 1927, **21**, 693; *Brit. Chem. Abs.* **A**, 1927, 11. G. S. Parks, K. K. Kelley and H. M. Huffman, *J.A.C.S.*, 1929, **51**, 1969; *Chem. Abs.*, 1929, **23**, 4877; *Brit. Chem. Abs.* **A**, 1929, 990. G. S. Parks, H. M. Huffman and S. B. Thomas, *J.A.C.S.*, 1930, **52**, 1032; *Brit. Chem. Abs.* **A**, 1930, 677; *Chem. Abs.*, 1930, **24**, 1839. H. M. Huffman, G. S. Parks and A. C. Daniels, *J.A.C.S.*, 1930, **52**, 1547; *Chem. Abs.*, 1930, **24**, 2664; *Brit Chem. Abs.* **A**, 1930, 677. H. M. Huffman, G. S. Parks and S B. Thomas, *J.A.C.S.*, 1930, **52**, 3241; *Brit. Chem. Abs.* **A**, 1930, 1253; *Chem. Abs.*, 1930, **24**, 4755. G. S. Parks and H. M. Huffman, *J.A.C.S.*, 1930, **52**, 4381; *Chem. Abs.*, 1931, **25**, 82; *Brit. Chem. Abs.* **A**, 1931, 42. H. M. Huffman, G. S. Parks and M. Barmore, *J.A.C.S.*, 1931, **53**, 3876; *Chem. Abs.*, 1931, **25**, 5889; *Brit. Chem. Abs.* **A**, 1931, 1363. G. S. Parks, H. M. Huffman and M. Barmore, *J.A.C.S.*, 1933, **55**, 2733; *Brit. Chem. Abs.* **A**, 1933, 905; *Chem. Abs.*, 1933, **27**, 3912. H. Banse and G S. Parks, *J.A.C.S.*, 1933, **55**, 3223; *Brit. Chem. Abs.* **A**, 1933, 1014; *Chem. Abs.*, 1933, **27**, 4473. G. S. Parks and D. W. Light, *J.A.C.S.*, 1934, **56**, 1511; *Brit. Chem. Abs.* **A**, 1934, 951; *Chem. Abs.*, 1934, **38**, 4973. C. J. Jacobs and G. S. Parks, *J.A.C.S.*, 1934, **56**, 1513; *Chem. Abs.*, 1934, **28**, 4973; *Brit. Chem. Abs.* **A**, 1934, 951. S. S. Todd and G. S. Parks, *J.A.C.S.*, 1936, **58**, 134; *Brit. Chem. Abs.* **A**, 1936, 278; *Chem. Abs.*, 1936, **30**, 2477; *J. Inst. Pet. Tech.*, 1936, **22**, 201A. G. S. Parks, S. S. Todd and W. A. Moore, *J.A.C.S.*, 1936, **58**, 398; *Chem. Abs*., 1936, **30**, 4387; *Brit. Chem. Abs.* **A**, 1936, 557. G. S Parks, S. S. Todd and C. H. Shomate, *J.A.C.S.*, 1936, **58**, 2505. See also G. S. Parks and H. M. Huffman. "The Free Energies of Some Organic Compounds." The Chemical Catalog Co., Inc., New York, **1932**, for a summary of approximately the first ten items of this series.

[35] G. S. Parks, *Chem. Rev.*, 1936, **18**, 325; *Chem. Abs*., 1936, **30**, 5113.

that in the practical use of free energy data the absolute magnitude and not the percentage error is the important factor.

TABLE 238.—*Molal Free Energies of Formation of Some Normal Paraffins.*

	State	S°_{298} E.U.[a]	ΔH°_{298} Cal.	ΔS°_{298} E.U.	ΔF°_{298} Cal.	Maximum Uncertainty (±) in ΔF°_{298} Cal.
Methane..........	g	44.46	−18,070	−19.36	−12,300	80
Ethane...........	g	55.0	−20,600	−41.4	−8,260	300
Propane..........	g	(64.7)	−25,390	−64.3	−6,220	300
n-Butane.........	g	74.4	−30,570	−87.2	−4,580	300
n-Pentane........	l	62.0	−42,230	−132.2	−2,820	500
n-Heptane........	l	78.5	−55,410	−180.9	−1,480	500
n-Octane.........	l	86.0	−62,260	−206.0	−850	600
n-Dodecane.......	l	118.2	−85,910	−304.1	+3,540	1,400

[a] E.U. is the abbreviation generally used for "entropy units" (cal. per degree absolute per mole).

These free energy values have been calculated by Parks[36] on the basis of the latest thermal data available, and supersede the respective figures previously given by Parks and Huffman.[37] The heats of combustion used for determining the heats of formation for all of these hydrocarbons except dodecane are the results of Rossini.[38] For the latter hydrocarbon (dodecane), the combustion data used is that of Banse and Parks[39] corrected according to the method of Washburn.[40] In calculating ΔS°_{298} for the formation of the hydrocarbons, Giauque's[41] value of 15.615 E.U. for $\frac{1}{2}H_2$ (obtained from spectroscopic determinations)[42] and that of Jacobs and Parks,[43] 1.36 E.U. for graphitic carbon, have been employed. The entropies of the hydrocarbons are from the following sources: that of methane is based on the results of statistical determinations of Giauque, Blue and Overstreet[44] and Kassel,[45] while that of ethane is the mean of third law estimates given by Parks and Huffman[46] and statistical determinations of Mayer, Brunauer and Mayer[47] and of Smith and Vaughan.[48] In the absence of any available entropy data for propane, Parks has obtained this value as a direct interpolation of the entropies of ethane and *n*-butane. The latter value and also that of dodecane are those of Huffman, Parks and Barmore.[49] For *n*-pentane, the figure is that of Parks and Huffman,[50] and for *n*-heptane and *n*-octane, the results are those of Parks, Huffman and Thomas.[51]

[36] G. S. Parks, *loc. cit.*

[37] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, 1932.

[38] F. D. Rossini, *Bur. Standards J. Research*, 1934, **13**, 21; *Brit. Chem. Abs.* **A**, 1934, 1071; *Chem. Abs.*, 1934, **28**, 6065.

[39] H. Banse and G. S. Parks, *J.A.C.S.*, 1933, **55**, 3223; *Chem. Abs.*, 1933, **27**, 4473; *Brit. Chem. Abs.* **A**, 1933, 1014.

[40] E. W. Washburn, *Bur. Standards J. Research*, 1933, **10**, 525; *Brit. Chem. Abs.* **A**, 1933, 676; *Chem. Abs.*, 1933, **27**, 2868.

[41] W. F. Giauque, *J.A.C.S.*, 1930, **52**, 4816; *Brit. Chem. Abs.* **A**, 1931, 294; *Chem. Abs.*, 1931, **25**, 867.

[42] The calculation of thermodynamic data from spectroscopic determinations has been discussed by L. S. Kassel (*Chem. Rev.*, 1936, **18**, 277; *Chem. Abs.*, 1936, **30**, 5112. The entropy values obtained in this manner are the so-called "absolute" entropies and contain terms which are not measured by specific heat methods, e.g., nuclear spin contributions. The term "entropy" as used in this text is the "practical" entropy, i.e., absolute entropy minus the nuclear spin entropy, or in other words, that quantity which would be obtained from specific heat measurements. See J. D. Kemp and K. S. Pitzer (*J. Chem. Phys.*, 1936, **4**, 749; *Chem. Abs.*, 1937, **31**, 28; *Brit. Chem. Abs.* **A**, 1937 (1), 21) for a discussion of this topic

[43] C. J. Jacobs and G. S. Parks, *J.A.C.S.*, 1934, **56**, 1513; *Chem. Abs.*, 1934, **28**, 4973; *Brit. Chem. Abs.* **A**, 1934, 951.

[44] W. F. Giauque, R. W. Blue and R. Overstreet, *Phys. Rev.*, 1931, **38**, 196; *Brit. Chem. Abs.* **A**, 1933, 453; *Chem. Abs.*, 1931, **25**, 5342.

[45] L. S. Kassel, *J.A.C.S.*, 1933, **55**, 1351; *Chem. Abs.*, 1933, **27**, 2611; *Brit. Chem. Abs.* **A**, 1933, 561.

[46] G. S. Parks and H. M. Huffman, *loc. cit.*

[47] J. E. Mayer, S. Brunauer and M. G. Mayer, *J.A.C.S.*, 1933, **55**, 37; *Brit. Chem. Abs.* **A**, 1933, 218; *Chem. Abs.*, 1933, **27**, 1263.

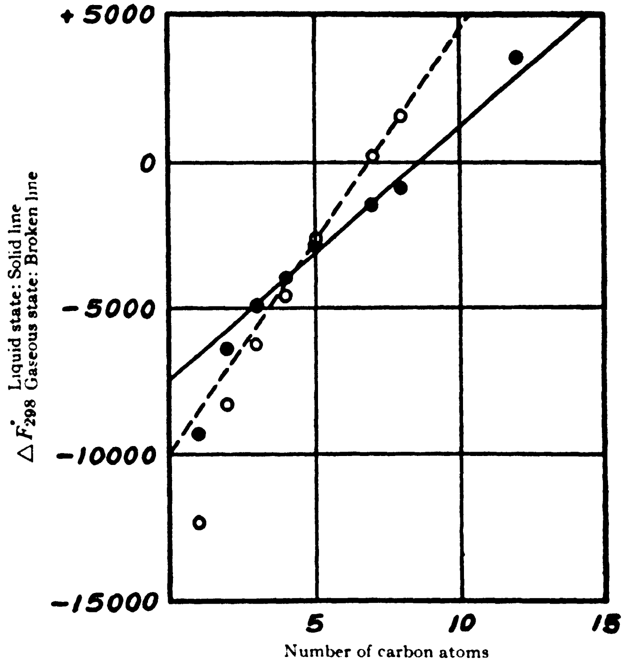
[48] H. A. Smith and W. E. Vaughan, *J. Chem. Phys.*, 1935, **3**, 341. *Chem. Abs.*, 1935, **29**, 4498; *Brit. Chem. Abs.* **A**, 1935, 934. In this connection see J. D. Kemp and K. S. Pitzer (*J. Chem. Phys.*, 1936, **4**, 749; *J.A.C.S.*, 1937, **59**, 276; *Chem. Abs.*, 1937, **31**, 28; *Brit. Chem. Abs.* **A**, 1937 (1), 21) and R. K. Witt and J. D. Kemp (*J.A.C.S.*, 1937, **59**, 273) for experimental and theoretical values of *S* for ethane

[49] H. M. Huffman, G. S. Parks and M. Barmore, *J.A.C.S.*, 1931, **53**, 3876; *Chem. Abs.*, 1931, **25**, 5889; *Brit. Chem. Abs.* **A**, 1931, 1363 .

[50] G. S. Parks and H. M. Huffman, *J.A.C.S.*, 1930, **52**, 4381; *Brit. Chem. Abs.* **A**, 1931, 42; *Chem. Abs.*, 1931, **25**, 82.

[51] G. S. Parks, H. M. Huffman and S. B Thomas, *J.A.C.S.*, 1930, **52**, 1032; *Chem. Abs.*, 1930, **24**, 1839; *Brit. Chem. Abs.* **A**, 1930, 677.

The regularities in the free energies of these hydrocarbons can be readily ascertained from Fig. 315. To facilitate the comparisons in the liquid state, Parks[52] has calculated the hypothetical values for methane (—9,300 cal.), ethane (—6,440 cal.), propane (—4,940 cal.) and *n*-butane (—3,950 cal.). Similarly, for the gaseous state, the theoretical free energies of *n*-pentane (—2,570 cal.), *n*-heptane (190 cal.) and *n*-octane (1,520 cal.) are included. From the graph, it will be seen that the free energies of the paraffins rise appreciably with increasing length of the carbon chain. Above propane the relation between ΔF°_{298} and *n*, the number of carbon atoms, is linear in each case. Thus, for liquid normal paraffins the increase in molal free energy is 860 cal. for each CH_2 increment, whereas for gaseous hydrocarbons it is 1,440 cal.



Courtesy Chemical Reviews, Williams and Wilkins Co.

FIG. 315.—Free Energies of Normal Paraffin Hydrocarbons. (G. S. Parks)

Branched Paraffins. According to Parks and Huffman[53] the molal free energy of the higher paraffins at 298.1°K. (25°C.) appears to increase slightly with increased branchiness of the paraffin, that is, the branched isomers are less stable thermodynamically than the corresponding normal compounds. Parks, Huffman and Thomas[54] have calculated the entropies of 8 isomers of *n*-heptane (2-methylhexane, 3-methylhexane, 3-ethylpentane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane and 2,2,3-trimethylbutane) and two of the isomers of *n*-octane (2,2,4-trimethylpentane and hexamethylethane) from low-temperature specific heat measurements in conjunction with the third law. The variations in the individual values of the free energies are rather small and, according to Parks,[55] in some cases not larger than the possible errors in combustion values. The differences between the free energy of the branched isomers and that of the *n*-hydrocarbons have been summarized by Parks and are given in Table 239.

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[52] G. S. Parks, *loc. cit.*

[53] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, 1932.

[54] G. S. Parks, H. M. Huffman and S. B. Thomas, *J.A.C.S.*, 1930, **52**, 1032; *Brit. Chem. Abs.* **A**, 1930, 677; *Chem. Abs.*, 1930, **24**, 1839. H. M. Huffman, G. S. Parks and S. B. Thomas, *J.A.C.S.*, 1930, **52**, 3241; *Brit. Chem. Abs.* **A**, 1930, 1253; *Chem. Abs.*, 1930, **24**, 4755.

TABLE 239.—*Effects of Branching on Free Energy of Paraffins (in Cal. Per Mole).*

	Number of Branches			
	1	2	3	4
Isoheptanes	0	+1,200	+2,200	
	+1,200	+1,700		
		+600		
Isooctanes			+2,200	+4,500
Average effect of a branch	+750			

Thus, from the table it will be seen that all of these increments, although rather irregular, do show a slight increase in molal free energy with increased branching, leading to a mean value of +750 cal. per branch (either methyl or ethyl group). In one case, however (2-methylpentane), the free energy of the isomer was found to be identical with that of the straight chain hydrocarbon. At first this was attributed to a fortuitous error which might have concealed an effect of only a few hundred calories. On the basis of more recent observations, Parks has suggested that this equality may be real, and that it is even possible that certain lower isoparaffins, such as isobutane, may have a slightly lower molal free energy than the normal compound.

Rossini[56] has calculated the heat of reaction for the transformation of *n*-butane to isobutane in the gaseous phase at 298.1°K. (25°C.) to be:

$$n\text{-}C_4H_{10(g)} = iso\text{-}C_4H_{10(g)};\ \Delta H^{\circ}_{298} = -1{,}630\ (\pm\ 150)\ \text{cal.}$$

Assuming an increase in ΔS°_{298} for this reaction to be —5 E.U. (in accordance with the method of Parks and Huffman[57]), Parks[58] has calculated the free energy change for the isomerization reaction to be $\Delta F = -140\ (\pm 150)$ cal. This figure would indicate that isobutane is slightly more stable thermodynamically than *n*-butane.

Unsaturated Aliphatic Hydrocarbons. The free energy data on the straight and branched unsaturated hydrocarbons are rather scanty. In the case of the olefins, the values on hand, however, do indicate that the effects of increasing length of chain and branching are essentially similar to those of the paraffins. Parks[59] has supplied the data for the first six olefins listed in Table 240. The results for 1,4-pentadiene, *n*-heptane-1 and the two isomers of diisobutylene[60] (that referred to as "low boiling" is thought to be 2,4,4-trimethylpentene-1 and the "high boiling" to be 2,4,4-trimethylpentene-2) have been obtained by Parks, Todd and Shomate[61] and are also included in this table, to which, for comparative purposes, Parks and Huffman's[62] values for acetylene have been added.

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[55] G. S. Parks, *Chem. Rev.*, 1936, **18**, 325; *Chem. Abs.*, 1936, **30**, 5113.

[56] F. D. Rossini, *J. Chem. Phys.*, 1935, **3**, 438; *Chem. Abs.*, 1935, **29**, 5730.

[57] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, **1932**, Chapters 3 and 12.

[58] G. S. Parks, *loc. cit.*

[59] G. S. Parks, *Chem. Rev.*, 1936, **18**, 325; *Chem. Abs.*, 1936, **30**, 5113.

[60] The diisobutylene mentioned by G. S. Parks and H. M. Huffman (*J.A.C.S.*, 1930, **52**, 4381; *Chem. Abs.*, 1931, **25**, 82; *Brit. Chem. Abs.* **A**, 1931, 42; also, *loc. cit.*) and again by G. S. Parks (*loc. cit.*) has been found to have been a mixture of isomers, predominantly of the lower boiling type.

TABLE 240.—*Molal Free Energies of Formation of Some Olefins and Acetylene.*

	State	S°_{298} E.U.	ΔH°_{298} Cal.	ΔS°_{298} E.U.	ΔF°_{298} Cal.	Maximum Uncertainty (±) in ΔF°_{298} Cal.
Ethylene.......	g	52.3	11,975	−12.9	+15,820	300
Propene.......	g	63.1	4,475	−34.7	14,820	300
Butene-1.......	g	72.5	−480	−57.9	16,780	600
cis-Butene-2....	g	73.0	−2,250	−57.4	14,860	500
trans-Butene-2 .	g	71.2	−3,200	−59.2	14,450	500
Isobutene......	g	69.0	−4,060	−61.4	14,240	500
1,4-Pentadiene .	l	58.2	18,060	−73.5	39,970	800
n-Heptene-1 ...	l	78.6	−25,520	−149.5	19,050	800
Diisobutylene (low boiling)..	l	73.2	−36,360	−187.5	19,530	1500
Diisobutylene (high boiling).	l	74.5	−35,250	−186.2	20,260	2000
Acetylene......	g	(48.1)	54,900	(+14.3)	50,840	500

The ΔF°_{298} for ethylene, propene, isobutene and the diisobutylenes represent replacements for the corresponding values of Parks and Huffman. For all of the olefins listed in this table, Parks and his collaborators have used ΔH°_{298} data derived from the heats of hydrogenation observed by Kistiakowsky, Romeyn, Ruhoff, Smith and Vaughan[63] and Kistiakowsky, Ruhoff, Smith and Vaughan[64] in conjunction with Rossini's[65] heats of formation for the corresponding paraffins. The entropy of ethylene represents the weighted mean of the results of Smith and Vaughan[66] and Kassel[67] (both obtained from spectroscopic data). In the case of propene, the entropy is that obtained by Huffman, Parks and Barmore.[68] The entropies and free energies of the four butenes are the results given by Todd and Parks[69] and the corresponding values for 1,4-pentadiene, *n*-heptene-1 and the two diisobutylenes, those of Parks, Todd and Shomate.[70] The molal entropies of graphitic carbon and of hydrogen are the values of Jacobs and Parks[71] and Giauque,[72] respectively, as were used in the calculations of Table 238.

In the case of acetylene, the heat of combustion is the mean of that given in the International Critical Tables[73] and that of Mixter.[74] The values of ΔF°_{298} are based on equilibrium measurements of von Wartenberg,[75] Pring[76] and Pring and Fairlie.[77] The entropy values estimated[78] by Parks and Huffman (identified in table by parentheses) give a corresponding free energy of acetylene of 50,640 cal.

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[61] G. S. Parks, S. S. Todd and C. H. Shomate, *J.A.C.S.*, 1936, **58**, 2505.

[62] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, **1932**.

[63] G. B. Kistiakowsky, H. Romeyn, Jr., J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J.A.C.S.*, 1935, **57**, 65; *Brit. Chem. Abs.* **A**, 1935, 304; *Chem Abs.*, 1935, **29**, 2065; *J. Inst. Pet. Tech.*, 1935, **21**, 89A.

[64] G. B. Kistiakowsky, J. R. Ruhoff, H A Smith and W. E. Vaughan, *J.A.C.S.*, 1935, **57**, 876; 1936, **58**, 137, 146; *J. Inst. Pet. Tech.*, 1935, **21**, 255A; *Chem. Abs.*, 1935, **29**, 4254; 1936, **30**, 1645, 1646; *Brit. Chem. Abs.* **A**, 1935, 1071.

[65] F. D. Rossini, *Bur. Standards J. Research*, 1934, **13**, 21; *Chem. Abs.*, 1934, **28**, 6065; *Brit. Chem. Abs.* **A**, 1934, 1071.

[66] H. A. Smith and W. E. Vaughan, *J. Chem. Phys.*, 1935, **3**, 341; *Brit. Chem. Abs.* **A**, 1935, 934; *Chem. Abs.*, 1935, **29**, 4998.

[67] L. S. Kassel, *J.A.C.S.*, 1933, **55**, 135; *Brit. Chem. Abs.* **A**, 1933, 218; *Chem. Abs.*, 1933, **27**, 2611.

[68] H. M. Huffman, G. S. Parks and M. Barmore, *J.A.C.S.*, 1931, **53**, 3876; *Chem. Abs.*, 1931, **25**, 5889; *Brit. Chem. Abs.* **A**, 1931, 1363.

[69] S. S. Todd and G. S. Parks, *J.A.C.S.*, 1936, **58**, 134; *Brit. Chem. Abs.* **A**, 1936, 278; *Chem. Abs.*, 1936, **30**, 2477; *J. Inst. Pet. Tech.*, 1936, **22**, 201A.

[70] G. S. Parks, S. S. Todd and C. H. Shomate, *loc. cit.*

[71] C. J. Jacobs and G. S. Parks, *J.A.C.S.*, 1934, **56**, 1513; *Chem. Abs.*, 1934, **28**, 4973; *Brit. Chem. Abs.* **A**, 1934, 951.

[72] W. F. Giauque, *J.A.C.S.*, 1930, **52**, 4816; *Brit. Chem. Abs.* **A**, 1931, 294; *Chem. Abs.*, 1931, **25**, 867.

[73] "International Critical Tables," McGraw-Hill Book Co., New York and London, **1926**, Volume *V*, 163.

[74] W. G. Mixter, *Am. J. Sci.*, 1906, (4) **22**, 13; *J.C.S.*, 1906, **90** (2), 598; *Chem. Zentr.*, 1906, **2**, 414.

[75] H. von Wartenberg, *Z. anorg. Chem.* 1907, **52**, 299; *Chem. Zentr.*, 1907, 1, 800; *J.C.S.*, 1907, **92** (1), 299.

[76] J. N. Pring, *J.C.S.*, 1906, **89**, 1601; 1910, **97**, 498; *Chem. Abs.*, 1910, **4**, 2111.

[77] J. N. Pring and D. M. Fairlie, *Ind. Eng. Chem.*, 1912, **4**, 812; *Chem. Abs.*, 1913, **7**, 307.

From their observations of the isomeric butenes, Todd and Parks[79] have shown that the position of the double bond and geometrical isomerism undoubtedly play important roles in the evaluation of the free energy. According to Parks[80] the introduction of one or more radicals as methyl groups to the carbon atoms adjacent to the double bond exerts a progressive protective action on the double bond. This may be in the form of "spatial screening," tending to render the olefin more like a paraffin hydrocarbon. However, the calculations of Parks, Todd and Shomate[81] on dehydrogenation reactions now furnish a quantitative estimate of this screening effect. According to these authorities, the free energy change for the formation of a normal 1-olefin by dehydrogenation of paraffins in accordance with the general equation:

$$n\text{-paraffin} \longrightarrow n\text{-olefin-1} + H_2$$

is apparently about 21,000 cal., irrespective of the length of carbon chain, except in the case of the ethane-ethylene combination.[82] The addition of other hydrocarbon chains to the carbon atoms adjacent to the double bond lowers the free energy value for the dehydrogenation and in the case of 2,4,4-trimethylpentene-1 (low boiling diisobutylene isomer) is 18,180 cal., according to these authorities. An analogous decrease in ΔF°_{298} when the double bond becomes more centrally located in the molecule was also noted by Todd and Parks in studying the isomeric butenes. For methylbutane to trimethylethylene and tetramethylethane to tetramethylethylene, Parks, Todd and Shomate estimate $\Delta F^\circ_{298} = 17{,}360$ and 17,100 cal., respectively, using heats of hydrogenation obtained by Kistiakowsky, Ruhoff, Smith and Vaughan.[83] The latter figure represents a free energy decrease of approximately 4000 cal. when compared with the normal 1-olefins. Therefore, it will be seen that the substitution of hydrocarbon chains for hydrogen atoms attached to a double bond causes the olefins to become thermodynamically more stable with respect to the corresponding saturated compounds.

The difference between the free energies of ethane and acetylene amounts to almost 60,000 cal. Unfortunately, experimental data on higher members of the acetylene series are entirely lacking, so that comparisons in this respect cannot be made. The exceptionally high value for the free energy (about 25,000 cal. per carbon atom) indicates that at 25°C. acetylene is thermodynamically very unstable with respect to decomposition into carbon and hydrogen.

Cyclic Hydrocarbons. In Table 241 have been summarized the free energies of formation of various cyclic compounds, all of which except cyclopentane (and its derivatives) have been calculated by Parks and Huffman.[84] In this table are included the basic thermal data and the maximum uncertainty in the free energy as estimated by these authorities. The possible errors are, in general, higher than those given in the two preceding free energy tables for paraffins and olefins, and may be attributed mostly to inaccuracies in the heat of combustion values.

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[78] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, **1932**, 86. These authorities estimated the absolute entropy of acetylene by subtracting twice the average value (2.7E.U.) observed for the decrease in entropy caused by the insertion of a double bond from the absolute entropy of ethane.

[79] S. S. Todd and G. S. Parks, *loc. cit.*

[80] G. S. Parks, *loc. cit.*

[81] G. S. Parks, S. S. Todd and C. H. Shomate, *J.A.C.S.*, 1936, **58**, 2505.

[82] The free energy values given by Parks (*Chem. Rev.*, 1936, **18**, 325; *Chem. Abs.*, 1936, **30**, 5113) for various dehydrogenations are: ethane to ethylene: 26.000 cal.; propane to propene: 21,040 cal.; and *n*-butane to butene-1: 21.360 cal. Parks, Todd and Shomate (*loc. cit.*) estimate the free energy change for the conversion of *n*-heptane to *n*-heptene-1 to be 20.620 cal. and for *n*-pentane to 1,4-pentadiene: 2 x 21,400 cal.

[83] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, *J.A.C.S.*, 1936, **58**, 137, 146; *Chem. Abs.*, 1936, **30**, 1645, 1646.

[84] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog., Inc., New York, **1932**.

TABLE 241.—*Molal Free Energies of Formation of Some Cyclic Hydrocarbons.*

	State	S°_{298} E.U.	ΔH°_{298} Cal.	ΔS°_{298} E.U.	ΔF°_{298} Cal.	Maximum Uncertainty (±) in ΔF°_{298} Cal.
Cyclopentane	1	49.4	−29,450	−113.5	4,400	2000
Methylcyclopentane	1	59.2	−37,800	−136.0	2,700	2000
1,2-Dimethylcyclopentane	1	64.5	−47,650	−163.2	1,000	2000
Cyclohexene	1	51.8	−15,290	−112.2	18,200	2000
Cyclohexane	1	49.2	−36,700	−146.0	6,800	1000
Methylcyclohexane	1	59.3	−46,550	−168.4	3,600	2000
Benzene	1	41.9	11,630	−59.4	29,400	1000
Toluene	1	52.4	2,180	−81.6	26,500	1000
Ethylbenzene	1	61.2	−5,070	−105.4	26,300	2000
o-Xylene	1	59.3	−4,670	−107.3	27,300	2000
m-Xylene	1	60.3	−4,670	−106.3	27,000	2000
p-Xylene	1	60.5	−8,470	−106.1	23,200	2000
Naphthalene	s	39.9	15,960	−98.0	45,200	1000

All of the values given above (except those of cyclopentane and its derivatives) represent revisions by Parks and Huffman of earlier work. The combustion data from which the heats of formation were calculated for the naphthenes, cyclohexene and naphthalene are taken from the International Critical Tables,[85] and for the benzenoid hydrocarbons, from the results of Swietoslawski and Bobinska.[86] The entropies of all of the hydrocarbons were calculated from low temperature heat capacity measurements, using the third law of thermodynamics. For cyclohexene and methylcyclohexane these entropy values were determined by Parks and Huffman.[87] The entropies of cyclohexane and toluene are those obtained by Parks, Huffman and Thomas[88] and Kelley,[89] respectively, and those of the other benzenoid hydrocarbons are from the work of Huffman, Parks and Daniels.[90] Giauque's[91] entropy for hydrogen (S°_{298} = 15.615 E.U. for $\frac{1}{2}H_2$) and that of Lewis, Gibson and Latimer[92] (1.3 E.U.) for graphitic carbon were employed in calculating the change in entropy for these hydrocarbons. All of the data on cyclopentane have been calculated by Jacobs and Parks[93] and that for methyl and dimethyl cyclopentane by Huffman, Parks and Barmore.[94]

In the case of all of the cyclic hydrocarbons given above, it will be seen that the thermodynamic stability is increased by the introduction of side chains (i.e., the molal free energy becomes less). With benzene and its various methyl derivatives, however, the effect is very pronounced, as is shown in Fig. 316, in which the molal free energies in the liquid state for benzene, toluene, the three xylenes, pseudocumene (1,2,4-trimethylbenzene), the three tetramethylbenzenes, pentamethylbenzene, and hexamethylbenzene are plotted against the number of side chains. The molal free energies of these compounds reach a minimum with the tetramethylbenzenes, and then increase, so that, according to Parks,[95] the effect of adding one methyl group is apparently the same as the addition of six.

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[85] "International Critical Tables," McGraw-Hill Book Co., New York and London, 1926, 5, 163.

[86] W. Swietoslawski and J. Bobinska, *J.A.C.S.*, 1927, **49**, 2478; *Brit. Chem. Abs.* **A**, 1927, 1142; *Chem. Abs.*, 1927, **21**, 3815.

[87] G. S. Parks and H. M. Huffman, *J.A.C.S.*, 1930, **52**, 4381; *Chem. Abs.*, 1931, **25**, 82; *Brit. Chem. Abs.* **A**, 1935, 42.

[88] G. S. Parks, H. M. Huffman and S. B. Thomas, *J.A.C.S.*, 1930, **52**, 1032; *Brit. Chem. Abs.* **A**, 1930, 677; *Chem. Abs.*, 1930, **24**, 1839.

[89] K. K. Kelley, *J.A.C.S.*, 1929, **51**, 2738; *Chem. Abs.*, 1929, **23**, 5403; *Brit. Chem. Abs.* **A**, 1929, 1373.

[90] H. M. Huffman, G. S. Parks and A. C. Daniels, *J.A.C.S.*, 1930, **52**, 1547; *Chem. Abs.*, 1930, **24**, 2664; *Brit. Chem. Abs.* **A**, 1930, 677.

[91] W. F. Giauque, *J.A.C.S.*, 1930, **52**, 4816; *Chem. Abs.*, 1931, **25**, 867; *Brit. Chem. Abs.* **A**, 1931, 294.

[92] G. N. Lewis, G. E. Gibson and W. M. Latimer, *J.A.C.S.*, 1922, **44**, 1008; *J.C.S.*, 1922, **122** (2), 471; *Chem. Abs.*, 1922, **16**, 2058.

[93] C. J. Jacobs and G. S. Parks, *J.A.C.S.*, 1934, **56**, 1513; *Chem. Abs.*, 1934, **28**, 4973; *Brit. Chem. Abs.* **A**, 1934, 951.

[94] H. M. Huffman, G. S. Parks and M. Barmore, *J.A.C.S.*, 1931, **53**, 3876; *Chem. Abs.*, 1931, **25**, 5889; *Brit. Chem. Abs.* **A**, 1931, 1363.

[95] G. S. Parks, *Ind. Eng. Chem.*, 1933, **25**, 887; *Chem. Abs.*, 1933, **27**, 4473; *Brit. Chem. Abs.* **A**, 1933, 1014.

The respective ΔF°_{298} values of cyclopentane and cyclohexane are not directly comparable as regards ring stability, because these compounds contain different numbers of carbon atoms. According to Parks and Huffman[96] on the basis of the free energy per carbon atom, the cyclopentane ring is slightly more stable than the cyclohexane ring. However, considering the rather large uncertainty in the free energy values, especially in the case of the former compound, this view may be subject to change.

Other Organic Compounds. That definite free energy relations exist among the organic compounds of carbon, hydrogen and oxygen is evidenced in Fig. 317 of Parks and Huffman.[97] In this graph, the molal free energies of some aliphatic compounds containing one or two atoms of oxygen are plotted against the number of carbon atoms. In each case, the free energy values of the substances in their standard states (25°C.) have been used, so that most apply to the liquid state. The introduction of oxygen into a compound results in a very marked lowering of the molal free energy, that is, oxygenated substances are much more stable thermodynamically than hydrocarbons of the same number of carbon atoms. In any homologous series, according to Parks and Huffman, the trend in the free energies is probably similar to that of the normal paraffins, especially after the first few members of the series have been passed.

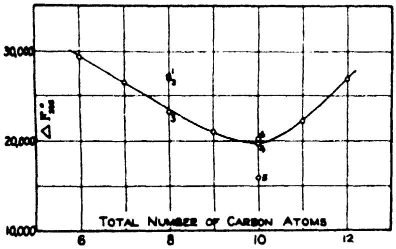

Fig. 316.
Free Energy Relations of Benzene and Its Methyl Derivatives. (G. S. Parks)

1. *o*-Xylene
2. *m*-Xylene
3. *p*-Xylene
4. Durene
5. Isodurene
6. Prehnitene

Courtesy Industrial and Engineering Chemistry

Estimation of Molal Entropy and Free Energy of Compounds from the Structure of the Molecule

Parks and Huffman[98] have pointed out the fairly regular changes in the molal entropy and free energy caused by variations in the structure of organic compounds. These generalizations are often helpful in predicting both entropy and free energy values of substances in the absence of actual experimental data. In the case of the hydrocarbons, the entropy and molecular structure are apparently related by a simple linear function. In this respect, the normal paraffins and cyclic hydrocarbons may be regarded as the basic structures. With regard to these thermodynamic properties, branched hydrocarbons are considered to be derivatives of

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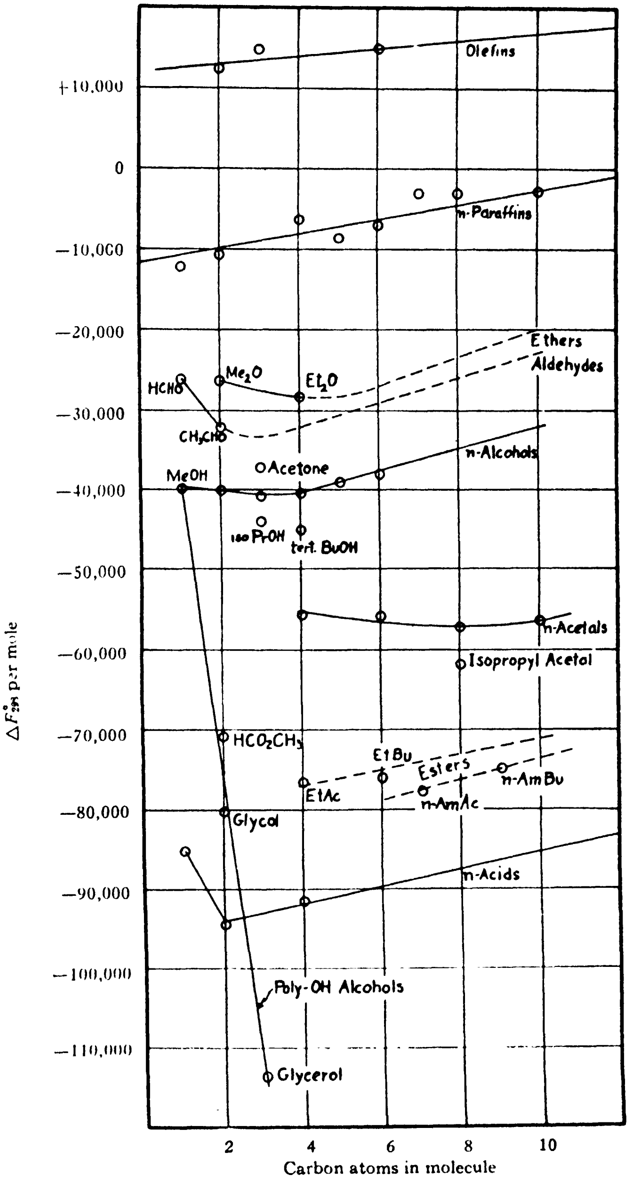
[96] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, 1932. See pp. 95-97 for a discussion of ring stabilities from the standpoint of thermodynamics.

[97] G. S. Parks and H. M. Huffman, *loc. cit.* Space does not permit a review of all the numerous prolific investigations of these authorities and their collaborators on the free energies and entropies of organic compounds. The generalities observed by Parks and Huffman allow an approximation of free energy values for a large number of substances in the absence of experimental data. For details, reference should be made to the above mentioned text.

[98] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, 1932, Chapter 12. G. S. Parks, *Ind. Eng. Chem.*, 1933, 25, 887; *Brit. Chem. Abs.* A, 1933, 1014; *Chem. Abs.*, 1933, 27, 4473. These deductions are based principally upon the data compiled by Parks and his collaborators in the series of articles listed in the section on Free Energy of Formation.



Courtesy Reinhold Publishing Corp.

FIG. 317.—Free Energy Relations Among Aliphatic Compounds Containing Oxygen. (G. S. Parks and H. M. Huffman)

the former type, in which one or more of the hydrogen atoms is replaced by methyl, ethyl or other aliphatic chains. Similarly, oxygen, nitrogen and halogen derivatives can be looked upon as substituted hydrocarbons. Using this method for olefins (viewed as dehydrogenated paraffins), the fluctuation in the predicted entropy values is greater than in the case of most other compounds. Still, especially with monolefins, the errors introduced are not of a very serious nature.

Theoretically, the comparisons between the various compounds should be made in the gaseous state, according to Parks,[99] in order to eliminate the effects of intermolecular attraction. However, the most practical basis is the liquid state, since most of the substances ordinarily studied are liquids at 25°C.[100]

Normal Paraffins. Parks, Huffman and Thomas[101] noted that for the normal paraffin hydrocarbons, the entropy could be expressed by the linear equation:

$$(1)\quad S_{298} = 25.0 + 7.7n$$

where n is the number of carbon atoms in the molecule. From this relation, 25.0 E.U.[102] may be regarded as the basic molal entropy for all of the normal paraffins in the liquid state. In the hypothetical case of liquid methane at 25°C. and 1 atmosphere pressure, the above equation gives

$$S_{298} = 25.0 + 7.7 = 32.7 \text{ E.U.}$$

and for heptane,

$$S_{298} = 25.0 + (7.7 \times 7) = 78.9 \text{ E.U.}$$

Huffman, Parks and Barmore[103] have continued these investigations and found that the differences between predicted and experimental values for molal entropies of various straight chain hydrocarbons were a maximum of about 1 per cent, although ordinarily the deviation was even much less. Fig. 318 shows the graphical representation of this function, plotted between the experimentally determined entropies and the number of carbon atoms in the straight chain.

In a similar manner, Parks and Huffman[104] have calculated that the entropy of normal paraffins in the gaseous state at 25°C. may be expressed as:

$$(2)\quad S_{298} = 34.0 + 10.0n$$

This equation, however, only applies to the first four members of the series which are normally gases at 25°C. and 1 atmosphere. They also suggest

$$(3)\quad S_{298} = 18.0 + 5.8n$$

for the estimation of the entropy of the normal crystalline paraffins.

Branched Paraffins. The substitution of a methyl group as a side chain

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[99] G. S. Parks, *loc. cit.*

[100] In a few cases where the compound is normally crystalline in its standard state, the procedure of H. M. Huffman, G. S. Parks and A. C. Daniels (*J.A.C.S.*, 1930, 52, 1547; *Chem. Abs.*, 1930, 24, 4755; *Brit. Chem. Abs.* A, 1930, 677) may be employed. The formula for the calculation of the change in entropy of fusion at 25°C. (ΔS_{298}) is:

$$\Delta S_{298} = \frac{\Delta H_{\text{fusion}}}{T_M} - \Delta C_p \ln \frac{T_M}{298.1}$$

where ΔH_{fusion} is the molal heat of fusion in calories and T_M is the melting point, in degrees absolute. These investigators suggest the value 0.05 times the molecular weight for ΔC_p, the difference between the molal heat capacities of the liquid and crystals. This entropy change is added to S_{298} of the liquid to give the corresponding S_{298} for the substances in the solid state.

[101] G. S. Parks, H. M. Huffman and S. B. Thomas, *J.A.C.S.*, 1930, 52, 1032; *Brit. Chem. Abs.* A, 1930, 677; *Chem. Abs.*, 1930, 24, 1839.

[102] E.U. is the abbreviation used for entropy units (calories per degree absolute per mole).

[103] H. M. Huffman, G. S. Parks and M. Barmore, *J.A.C.S.*, 1931, 53, 3876; *Chem. Abs.*, 1931, 25, 5889; *Brit. Chem. Abs.* A, 1931, 1363.

[104] G. S. Parks and H. M. Huffman, *loc. cit.*

for a methylene group in a paraffin molecule is accompanied by a decrease of about 4.5 E.U. per branch in the liquid state, according to Parks, Huffman and Thomas.[105] Thus, the preceding formula may be modified to give:

$$(4)\ S_{298} = 25.0 + 7.7n - 4.5r$$

where n is the total number of carbon atoms in the molecule and r is the number of methyl or aliphatic side chains. These investigators report predicted results in good agreement with observed values for the entropy of the eight isomers of *n*-heptane, 2-methylbutane and 2,2,4-trimethylpentane. Fig. 319 shows the experimentally determined molal entropies of seven of the isomeric heptanes plotted against r, the number of branches in the molecule.

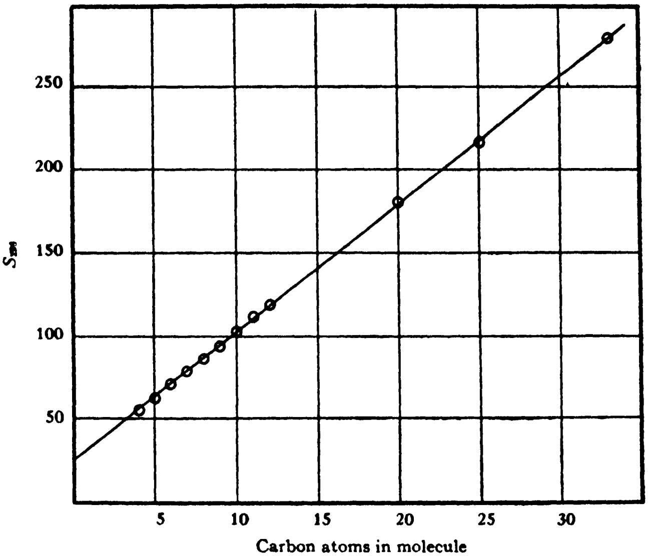

FIG. 318.—Molal Entropies of Normal Paraffin Hydrocarbons, (H. M. Huffman, G. S. Parks and M. Barmore)

Courtesy Journal of American Chemical Society

Aromatic Substituted Hydrocarbons. Huffman, Parks and Daniels[106] revised the above formula to apply to molecules involving phenyl groups, and suggested:

$$(5)\ S_{298} = 25.0 + 7.7n - 4.5r + 19.5p$$

where n is the number of carbon atoms not including the benzene ring, p is the number of phenyl groups in the compound and r is the number of hydrocarbon groups (aliphatic or aromatic, in this case) in excess of two attached to any carbon atoms in the aliphatic chain.[107] These investigators report good agreement between observed and calculated entropies for ethyl benzene, the xylenes, *ter*-butylbenzene, hexamethylbenzene (liquid), diphenylmethane (liquid), triphenylmethane (liquid) and bibenzyl (liquid).[108] That the relation between the molal entropies of the liquid benzenoid hydrocarbons and n, the number of carbon atoms outside the benzene nucleus, is a straight line will be seen from Fig. 320. In this figure, the S_{298} values of benzene, toluene, the three xylenes, pseudocumene (1,3,4-trimethylbenzene), n-butylbenzene, the three tetramethylbenzenes, pentamethylbenzene and hexamethylbenzene have been plotted against the number of carbon atoms outside the benzene ring. According to Parks[109] the somewhat low values for the first and last hydrocarbons may be attributed to the marked symmetry of the molecules involved.

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[105] G. S. Parks, H. M. Huffman and S. B. Thomas, *J.A.C.S.*, 1930, **52**, 1032; *Brit. Chem. Abs.* **A**, 1930, 677; *Chem. Abs.*, 1930, **24**, 1839.

[106] H. M. Huffman, G. S. Parks and A. C. Daniels, *J.A.C.S.*, 1930, **52**, 1547; *Brit. Chem. Abs.* **A**, 1930, 677; *Chem. Abs.*, 1930, **24**, 2664.

[107] As examples, for *ter*-butylbenzene, n is 4, r is 2 and p is 1; for triphenylmethane, n is 1, r is 1 and p is 3; and for toluene, n is 1, p is 1 and r is 0.

[108] In the case of biphenyl, the observed and calculated values differ by 4 E.U. (about 7 per cent). This may be attributed to too low a value for the heat of fusion, according to H. M. Huffman, G. S. Parks and A. C. Daniels (*loc. cit.*). With benzene (observed S_{298} = 41.9 E.U.) the discrepancy is 2.6 E.U. or about 6 per cent, due probably to its symmetry and unique character, as these authorities state.

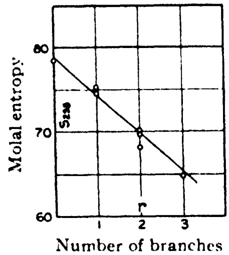

FIG. 319.
Influence of Number of Branch Chains in Molecule on Molal Entropies of Isomeric Heptanes. (G. S. Parks)

Courtesy Industrial and Engineering Chemistry

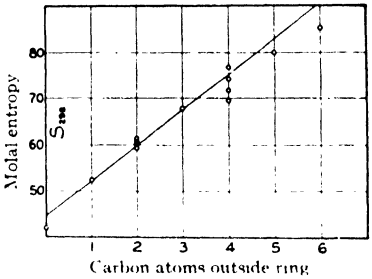

FIG. 320.
Molal Entropies of Liquid Benzenoid Hydrocarbons. (G. S. Parks)

Courtesy Industrial and Engineering Chemistry

Cycloparaffin Substituted Hydrocarbons. By means of a further addition to the last equation, Parks and Huffman have been able to apply it to liquid compounds involving cyclic hydrocarbons, such as cyclopentane and cyclohexane derivatives:

$$(6)\ S_{298} = 25.0 + 7.7n - 4.5r + 19.5p + 26.5p'$$

where n, p and r are the same quantities as above and p' is the number of saturated cyclopentane or cyclohexane rings. Parks calls attention to the fact that the experimentally measured entropy of cyclohexane (49.2 E.U.) is low in comparison with that of methylcyclohexane (59.3 E.U.), on account of the symmetry of the former hydrocarbon.[110]

Olefins. The differences observed in the entropies of various saturated compounds and the corresponding unsaturated ones led Parks and Huffman[111] to propose the additional term, $-2.7e$, to the general entropy equation for liquid hydrocarbons (where e designates the number of double bonds in the molecule). Although this was the average decrease per olefin bond obtained in six cases (pertaining mostly to crystalline unsaturated acids and various cyclic compounds), these investigators stated that, at best, it was only a rough estimation, and lacked the precision of the other terms in the general equation. They further point out that the effect was probably dependent to some extent upon the position of the double bond within the molecule and also upon the influence of neighboring groups. Subsequently, Todd and Parks[112] showed this to be the case in their study of isomeric butenes. However, the latter investigators further noted that the configuration of the molecule must also be considered. Table 242 gives the molal entropies of *cis*- and *trans*-2-butene and isobutene, as determined by Todd and Parks.

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[109] G. S. Parks, *Ind. Eng. Chem.*, 1933, **25**, 877; *Brit. Chem. Abs.* **A**, 1933, 1014; *Chem. Abs.*, 1933, **27**, 4473.

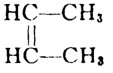
[110] These values were obtained by G. S. Parks, H. M. Huffman and S. B. Thomas, *J.A.C.S.*, 1930, **52**, 1032; *Chem. Abs.*, 1930, **24**, 1839; *Brit. Chem. Abs.* **A**, 1930, 677; and G. S. Parks and H. M. Huffman, *J.A.C.S.*, 1930, **52**, 4381; *Chem. Abs.*, 1931, **25**, 82; *Brit. Chem. Abs.* **A**, 1931, 42.

[111] G. S. Parks and H. M. Huffman, *J.A.C.S.*, 1930, **52**, 4381; *Chem. Abs.*, 1931, **25**, 82; *Brit. Chem. Abs.* **A**, 1931, 42.

TABLE 242.—*Molal Entropies of Three Isomeric Butenes.*

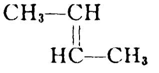
	cis-2-Butene	*trans*-2-Butene	Isobutene
Crystals (0 to 90°K.)	11.70	10.23	10.81
Crystals (above 90°K.)	6.55	11.18	6.17
Fusion	13.06	14.07	10.68
Liquid	19.57	13.61	18.72
Vaporization	20.63	20.41	20.33
Gas (to 298.1°K.)	1.50	1.70	2.29
Absolute Entropy, S°_{298}	73.0	71.2	69.0

Thus, the absolute entropy of the *cis* compound is 1.8 E.U. greater than that of



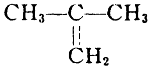
$$\begin{array}{c}HC{-}CH_3\\ \|\\ HC{-}CH_3\end{array}$$

cis-2-butene



$$\begin{array}{c}CH_3{-}CH\\ \|\\ HC{-}CH_3\end{array}$$

trans-2-butene



$$\begin{array}{c}CH_3{-}C{-}CH_3\\ \|\\ CH_2\end{array}$$

isobutene

its stereoisomer, the *trans* modification, and 4.0 E.U. higher than that of isobutene.[113]

The researches of Parks, Todd and Shomate[114] on the heat capacities of some higher olefins (namely *n*-heptene-1, 1,4-pentadiene, and two isomers of diisobutylene) also indicate that the molal entropy is largely dependent upon the symmetry of the molecule and the position of the double bond.[115] The average decrease per olefin bond in these determinations was found to be about 1.4 E.U. per mole. According to these authorities, although this figure cannot be considered very significant, it is probably preferable to the decrease of 2.7 E.U. suggested previously by Parks and Huffman.

Extension to Other Compounds. By means of the above equations, the molal entropy of the various hydrocarbons may be calculated. Parks and Huffman,[116] however, have carried this matter further. On the basis that oxygen, nitrogen and halogen compounds can be considered as derivatives of the various hydrocarbons and by comparisons with experimental data obtained in numerous investigations, these authorities formulated several general rules concerning the relation of entropy and structure. Their deductions, though purely empirical, permit the ready estimation of the S_{298} values for an enormous number of organic compounds, together with the approximate changes in ΔF°_{298} which may be expected due to these structures. Table 243 lists these results of Parks and Huffman.

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[112] S. S. Todd and G. S. Parks, *J.A.C.S.*, 1936, **58**, 134; *Brit. Chem. Abs.* **A**, 1936, 278; *Chem. Abs.*, 1936, **30**, 2477; *J. Inst. Pet Tech.*, 1936, **22**, 201A.

[113] In these experiments, tests were also made on 1-butene which, however, failed to crystallize even at 81.3°K. (−191.8°C.). Todd and Parks estimated the absolute entropy of this isomer to be 72.5 ± 1.3 E.U. per mole.

[114] G. S. Parks, S. S. Todd and C. H. Shomate, *J.A.C.S.*, 1936, **58**, 2505.

[115] See also L. S. Kassel (*J. Chem. Physics*, 1936, **4**, 435; *Chem. Abs.*, 1936, **30**, 5844) for a discussion of the absolute entropies of olefins from spectroscopic determinations, which results are in fairly good agreement with Third Law measurements.

[116] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, **1932**.

TABLE 243.—*The Changes in Molal Entropy and Free Energy Accompanying Various Structural Modifications at 298.1°K.**

	—Change in Molal Entropy—			–Change in–
	Solid	Liquid	Gaseous	ΔF_{298}
Insertion of CH_2 into a hydrocarbon chain	5.8	7.7	10.0	1,080
Substitution of CH_3 for H attached to a main hydrocarbon chain	5.0 (?)	3.2	5.0 (?)	1,900
Substitution of C_2H_5 for H attached to a main hydrocarbon chain	—	10.9	—	3,000
Substitution of CH_3 for H in a hydrocarbon ring	5.8	7.7	—	0 (?)
Substitution of a phenyl group for H attached to carbon	17.0	19.5	—	36,000
Substitution of a cyclohexane or cyclopentane ring for H attached to carbon	—	26.5	—	13,000
Conversion of a single bond into an ethylenic double bond	−2.7	−2.7	−2.7	(a)
Substitution of OH for H to form a monohydroxy, primary alcohol	0 (?)	−1.5	13.0	−34,000
Substitution of OH for H to form a monohydroxy, secondary alcohol	0.5 (?)	−4.0	9.0 (?)	−37,000
Substitution of OH for H to form a monohydroxy, tertiary alcohol	0.5 (?)	−6.0	7.0 (?)	−41,000
Substitution of OH for H to form a phenol	0.0	0 (?)	—	−41,000
Substitution of OH for H to form polyhydroxy compounds	0.5 (?)	0.5 (?)	—	(b)
Insertion of —O— linkage in a chain to form an ether	—	5.0	8.0	−20,000 (?)
Substitution of O for 2H to form an aldehyde	1.0 (?)	5.0 (?)	7.3 (?)	−23,000 (?)
Substitution of O for 2H to form a ketone	1.0	0.5 (?)	6.0	−30,000 (?)
Insertion of CO_2H for H to form a carboxylic acid	5.8	7.7	—	−83,200
Insertion of CO_2 group into a hydrocarbon chain to form an ester	—	13.2	21.0	−70,000
Substitution of NH_2 for H to form an amine	0.0	0.0	—	6,000
Substitution of NO_2 for H to form a nitro compound	7.0	8.0	—	7,000
Substitution of Cl for H	6.0	7.0 (?)	9.0 (?)	−1,600
Substitution of Br for H	7.5	9.0 (?)	11.5 (?)	4,500 (?)
Substitution of I for H	9.0 (?)	11.0 (?)	14.0 (?)	10,000 (?)
Substitution of bivalent S for O in a compound	2.0 (?)	2.0 (?)	2.0 (?)	36,000 (?)

? = Values marked in this manner are regarded as doubtful by Parks and Huffman.

[a] = Very irregular, mean about 20,000.

[b] = Primary OH, −34,000; secondary OH, −37,000

* G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, 1932.

As an example in the use of these data, the entropy of 2,2,3-trimethylbutane may be considered. Using equation for liquid branched paraffins, $n = 7$ and $r = 3$. Therefore

$$S_{298} = 25.0 + (7.7 \times 7) - (4.5 \times 3) = 65.4 \text{ E.U.}$$

It will be noted that this procedure is equivalent to obtaining the entropy of liquid butane by means of equation (1) and adding the effect of the substitution of three methyl groups for hydrogen atoms, taken from Table 243. For instance:

$$S_{298} = 25.0 + (7.7\times4) = 55.8 \text{ E.U.}$$

for liquid butane. The substitutional effect is

$$(3\times3.2) = 9.6 \text{ E.U.}$$

Adding the two gives 65.4 E.U. This predicted value of S_{298} is within 1 per cent of that obtained experimentally (64.8 E.U.) for 2,2,3-trimethylbutane by Huffman, Parks and Thomas.[117] In a similar manner, S_{298} for solid palmitic acid (which Parks and Huffman regard as the derivative of *n*-pentadecane in which one hydrogen atom on the terminal carbon atom has been replaced by a carboxyl group) may be predicted. Thus, for solid *n*-pentadecane ($C_{15}H_{32}$) from equation (3),

$$S_{298} = 18.0 + (5.8\times15) = 105.0 \text{ E.U.}$$

Adding to this value 5.8 E.U. which is the effect for the carboxyl substitution, the resulting entropy value for solid palmitic acid is 110.8 E.U.[118]

VARIATION OF FREE ENERGY WITH TEMPERATURE

Although for convenience in comparisons free energy values are ordinarily tabulated at 298.1°K. (25°C.), a knowledge of the variation of free energy with temperature is important in the case of studies looking to various practical applications, since most reactions are carried out at temperatures other than room temperatures.

From the Gibbs-Helmholtz equation,[119] the change in free energy with respect to temperature at constant pressure may be expressed as:

$$(7)\ \Delta F^{\circ}_{T} = \Delta H_0 - \Delta aT\ln T - \tfrac{1}{2}\Delta bT^2 - \tfrac{1}{6}\Delta cT^3 + IT$$

where ΔF°_{T} is the free energy at the absolute temperature T, ΔH_0 is the basic heat of formation, Δa, Δb and Δc are the constants in the empirical equation for the increase in heat capacity at constant pressure:

$$\Delta C_p = \Delta a + \Delta bT + \Delta cT^2$$

and I is the integration constant.[120] When all of the constants can be evaluated, equation (7) may be used to give the free energy at any temperature. However, as Francis[121] has stated, equations of this nature are very awkward to employ. In general, the curves do not deviate considerably from a straight line, especially in the temperature range of 400-1000°K. (127-727°C.), and therefore Francis recommends the use of a linear function, such as:

$$(8)\ \Delta F = h + kT$$

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[117] H. M. Huffman, G. S. Parks and S. B. Thomas, *J.A.C.S.*, 1930, **52**, 3241; *Chem. Abs.*, 1930, **24**, 4755; *Brit. Chem. Abs.* **A**, 1930, 1253.

[118] G. S. Parks, K. K. Kelley and H. M. Huffman (*J.A.C.S.*, 1929, **51**, 1969; *Brit. Chem. Abs.* **A**, 1929, 990; *Chem. Abs.*, 1929, **23**, 4877) experimentally determined S_{298} for solid palmitic acid to be 113.7. These values differ by 2.5 per cent.

[119] A rigorous thermodynamic proof of this equation is beyond the scope of this volume. Reference should be made to G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York and London, **1923**; and H. S. Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York (second edition), **1930**.

[120] The heat content at any temperature T is given by:

$$\Delta H_T = \Delta H_0 + \Delta aT + \tfrac{1}{2}\Delta bT^2 + \tfrac{1}{3}\Delta cT^3$$

From a knowledge of the value of the heat of reaction and the necessary specific heat data, ΔH_0 can be evaluated. By substituting ΔF°_{298} and $T = 298$ in equation (7), I can be determined. For examples of the application of this equation to numerical data, see A. W. Francis, *Ind. Eng. Chem.*, 1928, **20**, 277; *Chem. Abs.*, 1928, **22**, 1131; *Brit. Chem. Abs.* **A**, 1928, 478; and G. S. Parks and H. M. Huffman, *loc. cit.*

[121] A. W. Francis, *Ind. Eng. Chem.*, 1928, **20**, 277, 283; *Chem. Abs.*, 1928, **22**, 1131, 1716; *Brit. Chem. Abs.* **A**, 1928, 478, 479.

where h and k are empirical constants. Equation (8), although only an approximation, is sufficiently accurate for most purposes.[122]

As a test for the similarity of these two equations, Parks and Huffman[123] have calculated the variation in the free energy of formation of ethane following the reaction:

$$(9)\ 2C_{(graph.)} + 3H_{2(g)} = C_2H_{6(g)};\ \Delta F^\circ_{298} = -10{,}700 \text{ cal.}$$

According to equation (7), ΔF°_T for this reaction may be expressed as:

$$(7a)\ \Delta F^\circ_T = -19{,}190 + 15.77T \ln T - 0.0046T^2 - 59.6\,T$$

while from equation

$$(8a)\ \Delta F^\circ_T = -26{,}700 + 51.0T$$

The values for the free energy of ethane at different temperatures, as calculated by these investigators from equations (7a) and (8a) are listed in Table 244.

TABLE 244.—*Free Energy of Ethane at Various Temperatures.*[a]

°K.	400	500	600	700	800	900
°C.	127	227	327	427	527	627
ΔF°_T by 7a	−6,140	−1,360	+3,650	+8,830	+14,150	+19,560
ΔF°_T by 8a	−6,300	−1,200	+3,900	+9,000	+14,100	+19,200
Difference	−160	+160	+250	+170	−50	−360

[a] G. S. Parks and H. M. Huffman. "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, 1932.

From the differences, it will be seen that over this range of temperature (127-627°C.) the results obtained by using the approximate linear relation vary from those of equation (7) by about 1 to 2 per cent, which are well within the limits of experimental error.

Table 245 giving the values of h and k in equation (8) for the variation of free energy of formation of various substances with the temperature has been summarized from data given by Parks and Huffman.[124] The resulting equations are applicable over a temperature range of about 400 to 1000°K. (127 to 727°C.) for substances in the gaseous state. Since these values are based on experimental data which are subject to revision due to inaccuracies in heats of combustion and formation, the probable error in the value of ΔF°_{298} as listed by these investigators is also included.[125]

By combinations of approximate free energy-temperature equations for various compounds, Parks and Huffman have estimated three general formulas for variation of free energy with both temperature and length of the carbon chain. These are:[126]

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[122] This is especially true when the uncertainty of the free energy values of some of the compounds involved is considered.

[123] G. S. Parks and H. M. Huffman, *loc. cit.*

[124] G. S. Parks and H. M. Huffman, *loc. cit.*

[125] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, 1932. The probable errors have been estimated by Parks and Huffman and represent the maximum uncertainty in the values given by them in their "Table of Free Energies," p. 231. A. W. Francis has compiled a somewhat similar table to show the variation of free energy and temperature. Unfortunately the ΔF and ΔH values available at that time (1928) were in error to such an extent that they have been superseded by more recent determinations. However, reference should be made to the two articles of Francis mentioned previously for a concise treatment and explanation of the practical application of the principles involved in the above calculations.

[126] For comparative purposes, the equations derived by A. W. Francis (*loc. cit.*) are:

Paraffins: $\Delta F^\circ = -13{,}300 - 7850n + 2.2T + 25.55nT$
Olefins: $\Delta F^\circ = 31{,}060 - 9400n - 39.5T + 25.5nT$
Naphthenes: $\Delta F^\circ = 12{,}900 - 8500n - 19.3T + 25.5nT$
Acetylenes: $\Delta F^\circ = 68{,}400 - 7000n - 61.9T + 25.5nT$
Alcohols: $\Delta F^\circ = -43{,}540 - 7010n + 24.2nT$

where n is the number of carbon atoms and T is the absolute temperature.

for normal paraffins in the gaseous state:

$$(10)\ \Delta F^{\circ}_{\mathrm{T}} = -14{,}700 - 6000n + 1.0T - 25.0nT$$

for normal 1-olefins (hexene-1, octene-1 and so forth):

$$(11)\ \Delta F^{\circ}_{\mathrm{T}} = 5700 - 6500(n - 2) + 21.1T - 24.0(n - 2)T$$

and for normal primary alcohols:

$$(12)\ \Delta F^{\circ}_{\mathrm{T}} = -57{,}000 - 6000(n - 2) + 59.8T + 25.0(n - 2)T$$

where n is the number of carbon atoms and T is the absolute temperature. Fig. 321 is a comparison of the variation of molal free energies of four six-carbon atom hydrocarbons, benzene, hexene-1, n-hexane and cyclohexane in the gaseous state. Although at 400°K. (127°C.) n-hexane is the most stable (indicated by the lower value of ΔF°) and benzene is the least stable, at 1300°K. (1027°C.) this condition is entirely reversed. Analogously, at the lower temperature cyclohexane is slightly more stable than 1-hexene, but above 900°K. (627°C.) the opposite is true.

TABLE 245.—*Constants for Evaluating Free Energy at Various Temperatures Using the General Equation:*

$$\Delta F^{\circ}_{\mathrm{T}} = h + kT$$

	h	k	Maximum Probable Error (±) in Fundamental Value of ΔF°_{298} Cal./Mole
Methane	−19,450	23.0	500
Acetylene	−54,900	−13.6	500
Ethylene	5,700	21.1	2,000
Ethane	−26,700	51.0	1,000
n-Hexene-1	−20,300	117.1	2,000
Cyclohexane	−33,600	136.4	1,000
Octane	−62,700	201.0	2,000
Benzene	17,900	41.7	1,000
Toluene	8,200	66.0	1,000
m-Xylene	1,700	91.6	2,000
Naphthalene	30,500	63.0	1,000
Anthracene	43,400	91.6	5,000
Methyl alcohol	−49,300	34.4	500
Ethyl alcohol	−57,000	59.8	2,000
Acetic acid	−105,300	47.1	2,000
Formaldehyde	−27,800	6.0	2,000

APPLICATIONS OF FREE ENERGY TO PROBLEMS OF THE PETROLEUM INDUSTRY

The possibilities of the application of free energy data to problems of the petroleum industry are by no means as limited as those which will be discussed in this chapter.[127] However, the examples here cited are of a rather general nature, and may be considered as more or less representative applications.[128]

For convenience, most thermodynamic calculations are based on reactions taking place in the gaseous state. One reason for this has been pointed out by Francis,[129] namely, that general equations can be set up to cover these types of transformations. On the other hand, liquid phase reactions cannot be represented by general equations. However, in the latter case, from a knowledge of the vapor pressure, fugacity[130] or activity[131] of the substance, specific equations to cover each reaction may be readily formulated.

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[127] Consult A. W. Francis and R. V. Kleinschmidt (*Oil and Gas J.*, 1929, 28 (29), 118; *Amer. Pet. Inst. Bull.*, 1930, III, 93; *J. Inst. Pet. Tech.*, 1930, 16, 3A; *Chem. Abs.*, 1930, 24, 2369) for a discussion of the applications of thermodynamics and its limitations.

[128] It should be noted that in some cases the free energy values that have been used are not the most recent calculations. Refinements such as these will, of course, lessen the amount of uncertainty.

[129] A. W. Francis, *Ind. Eng. Chem.*, 1928, 20, 277; *Chem. Abs.*, 1928, 22, 1131; *Brit. Chem. Abs.* A, 1928, 478.

In some instances certain reactions which normally would be accompanied by a slight increase in free energy can be forced to proceed by the application of pressure, especially if the transformation is accompanied by a decrease in volume. However, Francis[132] has stated that even the use of high pressures will not ordinarily overcome an unfavorable free-energy change of more than about +5000 cal. Still another point emphasized by Francis is that a reaction which is found to be thermodynamically impossible (one in which the free energy change has a value of +10,000 cal. or higher, in a positive sense) cannot be induced to proceed by means of a catalyst.[133]

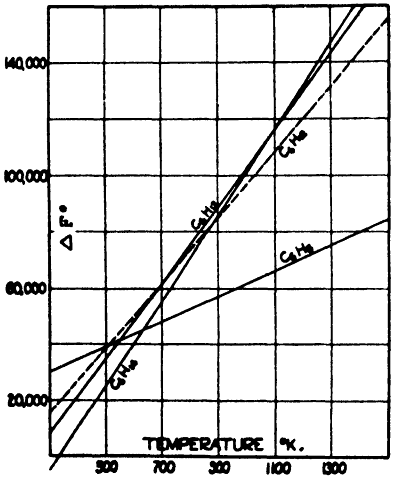

FIG. 321.
Variation of Molal Free Energies of Gaseous *n*-Hexane, 1-Hexene, Cyclohexane and Benzene as Function of Absolute Temperature. (G. S. Parks)

Courtesy Industrial and Engineering Chemistry

At this time it might also be well to restate some of the limitations of thermodynamics. Free energy calculations are based primarily on the concept of equilibrium. In actual practice, especially in cracking, true equilibrium is never attained, but according to Francis, only a condition nearer to this state is reached, and this implies a lower value of free energy. Furthermore, since the important variable, time, does not enter into thermodynamic considerations, no inkling as to the necessary duration for equilibrium to be established is possible. Many reactions appear to occur by concatenation, that is, by chain mechanisms, or by stepwise manners. In these cases, reaction rates, which likewise are beyond the scope of this science, play an important and perhaps even a predominating role.[134] Finally, it should also be remembered that the standard free energy values apply to substances in their standard state (one atmosphere pressure and 25°C.). The actual free energies of substances involved in reactions may differ appreciably from those under the assumed ideal conditions, and therefore should be corrected to the corresponding circumstances.[135]

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[130] Fugacity may be regarded as a corrected or effective vapor-pressure, i.e., the actual vapor pressure of a substance as differentiated from the theoretical vapor pressure that would be expected from calculations involving the use of the ideal gas laws. See G. N. Lewis and M. Randall ("Thermodynamics," McGraw-Hill Book Co., Inc., New York and London, 1923) for a discussion of this concept.

[131] Activity is a corrected or effective concentration, made necessary due to deviations of actual substances from ideality, usually applied to substances in the liquid state. See G. N. Lewis and M. Randall, *loc. cit.*

[132] A. W. Francis, *loc. cit.*

[133] In this respect, the possible error in the value of the free energy figures as given in the preceding table should be borne in mind. Thus, if the free energy of a reaction has been calculated to be 10,000 cal., but due to uncertainties in the free energies of formation that are involved (which errors may either be accumulative or compensating) there may be a factor of ± 5000 cal. to be considered. The above statement is of necessity subject to revision, as the free energy change for the reaction probably lies between +15,000 and +5000 cal., and if the latter value is the correct one, the reaction may proceed with catalysts.

Bearing the above discussion in mind, examples of the use of free energy calculations in cracking, hydrogenation and dehydrogenation, polymerization, the preparation of olefins, isomerization, the hydration of olefins, the Fischer synthesis and a few other general applications will be reviewed.[135a]

Cracking. A general discussion of the thermodynamics of cracking in reference to the work of Schultze[136] has already been given. Parks and Huffman[137] have also studied the application of this science to typical cracking reactions. Table 246 has been compiled from their calculations, and represents four types of rupture for *n*-tetradecane in the gaseous phase. The approximate equation expressing the free energy change with temperature is given in the first column, and in the second and third are listed the corresponding free energies at 600°K. (620°F.) and 1000°K. (1340°F.), respectively.

TABLE 246.—*Free Energy Changes for the Vapor Phase Cracking of n-Tetradecane.*

	ΔF°_T	ΔF°_{600} (620°F.)	ΔF°_{1000} (1340°F.)
(13) $C_{14}H_{30} = C_{12}H_{26} + CH_4 + C$..........	$-7,450 - 27T$	$-23,600$	$-34,400$
(14) $C_{14}H_{30} = C_8H_{18} + C_6H_{12}$ (hexene).....	$15,700 - 33T$	$-4,000$	$-17,200$
(15) $C_{14}H_{30} = C_8H_{18} + C_6H_{12}$ (cyclohexane).	$2,400 - 13.6T$	$-5,800$	$-11,200$
(16) $C_{14}H_{30} = C_8H_{18} + C_6H_6 + 3H_2$........	$53,900 - 108T$	$-11,100$	$-54,400$

Reaction (13) involves cracking to a lower paraffin with the simultaneous formation of methane and the deposition of carbon. In equation (14) the decomposition is to *n*-octane and hexene. In equations (15) and (16) the products are *n*-octane and cyclohexane and *n*-octane, benzene and hydrogen, respectively.

Concerning these reactions, all of which are thermodynamically feasible as indicated by the large negative values of ΔF° even at 600°K. (620°F.), it is impossible to predict just which one will predominate at any particular temperature. This is a typical case in which a knowledge of the various rates of reaction is required to establish the point. Thus, by use of specific catalysts, any one of these reactions might become the predominating one. Again, it is necessary to remember the equilibrium conditions assumed, and since these conditions cannot be attained, the corresponding free energy values should be somewhat lower. Parks and Huffman, however, suggest that in the absence of any data on the reaction rates, the magnitude of the free energy change may be taken as a crude criterion for the relative importance. In accordance with this assumption, at 600°K. (327°C.)

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[134] This matter will be discussed in more detail later in this chapter.

[135] In view of the magnitude of the uncertainty of most free energy values for organic compounds, this procedure is ordinarily not required. However, for the exact application of thermodynamics, corrections of this nature should be made. See G. N. Lewis and M. Randall, *loc. cit.*; and H. S. Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Co., Inc., New York, **1930**.

[135a] Evaluation of chemical reactions from the standpoint of thermodynamics has also been given consideration in previous portions of this text. Note especially Chapters 3, 26, 36 and 52.

[136] G. R. Schultze, *Angew. Chem.*, 1936, **49**, 268; *Chem. Abs.*, 1936, **30**, 6176; *Brit. Chem. Abs.* **B**, 1936, 535. See Chapter 3. This work of Schultze was based primarily on the general formulas of G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, **1932**.

[137] G. S. Parks and H. M. Huffman, *loc. cit.* Consult H. L. Hays (*Oil and Gas J.*, 1936, **34** (49), 39; *Chem. Abs.*, 1936, **30**, 5401) for a thermodynamic analysis of the reactions involved in cracking lower hydrocarbons, such as propane. Also M. W. Travers, *J. Inst. Fuel*, 1935, **8**, 157; *Brit. Chem. Chem. Abs.* **B**, 1935, 391; *Chem. Abs.*, 1935, **29**, 7935.

equation (13) might be expected to predominate and at 1000°K. (727°C.), equation (16).

Francis[138] has stated that liquid-phase cracking reactions are accompanied by lower free energy values, indicating slightly less thermodynamic favorability. The values for the corresponding liquid-phase reactions may be calculated, provided the partial pressures of the compounds involved are known.

Dehydrogenation. The change in ΔF accompanying the dehydrogenation of the lower paraffins has been investigated by Frey and Huppke.[139] These investigators obtained the necessary experimental data from equilibrium constant measurements at various temperatures, using an air-dried chromic oxide gel catalyst. Table 247 gives their equations for the change in ΔF for the dehydrogenation reactions and the value of ΔF at 673°K. (400°C.).

TABLE 247.—*Free Energies of Dehydrogenation of Lower Paraffins.*

	ΔF_T	ΔF_{673} (400°C.)
$C_2H_6 = C_2H_4 + H_2$	$27,798 - 9.21T \log T + 2.17T$	11,730
$C_3H_8 = C_3H_6 + H_2$	$25,920 - 9.21T \log T - 0.21T$	8,250
$n\text{-}C_4H_{10} = C_2H_5CH{=}CH_2 + H_2$	$25,790 - 9.21T \log T - 0.21T$	8,120
$n\text{-}C_4H_{10} = cis\text{-}CH_3CH{=}CHCH_3 + H_2$	$25,580 - 9.21T \log T - 0.21T$	7,910
$n\text{-}C_4H_{10} = trans\text{-}CH_3CH{=}CHCH_3 + H_2$	$25,090 - 9.21T \log T - 0.21T$	7,420
$iso\text{-}C_4H_{10} = (CH_3)_2C{=}CH_2 + H_2$	$23,900 - 9.21T \log T - 0.21T$	6,230

According to Frey and Huppke, the error in ΔF over the range of 300 to 600°C. is in no case more than several hundred calories. From their values of ΔF_{673} (400°C.) it will be seen that the dehydrogenation of the lower members of the paraffin series proceeds to only a very limited extent, even under equilibrium conditions and using a selective catalyst. At higher temperatures, especially in the case of the large molecular weight hydrocarbons, Frey and Huppke conclude that this type of decomposition may be expected.

Hydrogenation. The theoretical thermodynamic considerations of the hydrogenation of unsaturated hydrocarbons have been discussed by Sweeney and Voorhies.[140] For the hydrogenation[141] of benzene to cyclohexane, for instance, the standard free energy change may be represented by:

$$(17)\quad C_6H_{6(g)} + 3H_{2(g)} = C_6H_{12(g)};\ \Delta F_T^{\circ} = -51,500 + 94.7T$$

where T is the absolute temperature and each substance is assumed to be at 1 atmosphere pressure. At other partial pressures[142] (designated by p) of the three reactants, the above equation takes the form:

$$(18)\quad \Delta F = -51,500 + 94.7T + RT \ln \frac{p_{C_6H_{12}}}{p_{C_6H_6} \cdot p^3_{H_2}}$$

When equilibrium is attained in the system ($\Delta F = 0$), rearrangement of equation (18) gives:

$$(19)\quad \log \frac{p_{C_6H_{12}}}{p_{C_6H_6}} = \frac{11,250}{T} - 20.7 + 3 \log p_{H_2}$$

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[138] A. W. Francis, *Ind. Eng. Chem.*, 1928, **20**, 277; *Chem. Abs.*, 1928, **22**, 1131; *Brit. Chem. Abs.* **A**, 1928, 478.

[139] F. E. Frey and W. F. Huppke, *Ind. Eng. Chem.*, 1933, **25**, 54; *Chem. Abs.*, 1933, **27**, 654; *Brit. Chem. Abs.* **A**, 1933, 227. See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**, for a discussion of this work.

[140] W. J. Sweeney and A. Voorhies, Jr., *Ind. Eng. Chem.*, 1934, **26**, 195; *Chem. Abs.*, 1934, **28**, 2168; *Brit. Chem. Abs.* **B**, 1934, 438; *J. Inst. Pet. Tech.*, 1934, **20**, 165A.

[141] For a general discussion of hydrogenation of oils, see E. J. Gohr and R. P. Russell, *J. Inst. Pet. Tech.*, 1932, **18**, 595, 358A; *Chem. Abs.*, 1932, **26**, 4941; *Brit. Chem. Abs.* **B**, 1932, 919.

[142] This procedure is based on ideal conditions, i.e., assumption that the ideal gas laws hold. For high pressures, the fugacity, or effective pressure should be substituted. See G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York and London, **1923**.

Sweeney and Voorhies have substituted values of $T = 672°K.$ (750°F.) and 812°K. (1000°F.) in equation (19) and plotted the functions, as shown in Fig. 322. Thus, it is evident that the equilibrium ratio of cyclohexane to benzene increases sharply in proportion to the rise in hydrogen pressure. At 750°F. this quotient is 0.0001, corresponding to 1 atmosphere of hydrogen. At the same temperature and 150 atmospheres of hydrogen, the ratio of the partial pressure of cyclohexane to benzene is approximately 300. Thus, according to these investigators, it should be theoretically possible to obtain any degree of hydrogenation at a certain temperature by the appropriate choice of hydrogen pressure.

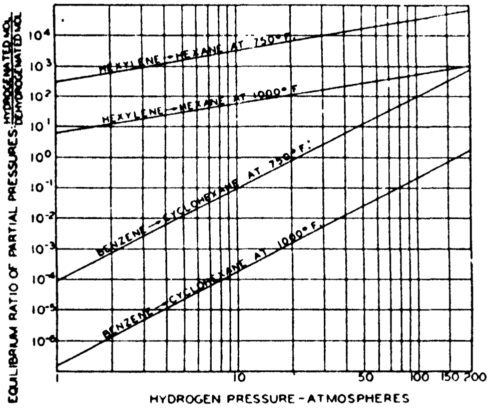

FIG. 322.
Effect of Temperature and Pressure in Simple Hydrogenation of Benzene and Hexene. (W. J. Sweeney and A. Voorhies)

Courtesy Industrial and Engineering Chemistry

The analogous case of the hydrogenation of hexene to hexane has also been discussed by Sweeney and Voorhies. When each of the substances is at 1 atmosphere pressure, the equation

$$C_6H_{12(g)} + H_{2(g)} = C_6H_{14(g)};\ \Delta F_T^\circ = -30{,}400 + 33.9T$$

gives the standard change in free energy. Likewise at other partial pressures of the three substances and at equilibrium, this transformation may be represented by:

$$\log \frac{p_{C_6H_{14}}}{p_{C_6H_{12}}} = \frac{6{,}650}{T} - 7.41 + \log p_{H_2}$$

Assuming the same temperatures as in the previous case, from Fig. 322 it will be seen that the equilibrium ratio of the partial pressures of hexane to hexene is greater than that of cyclohexane to benzene (in the preceding instance) indicating that the saturation of the olefin to give the corresponding paraffin should proceed quite readily even at 1 atmosphere pressure of hydrogen. The effect of hydrogen pressure is less pronounced in the case of the hexene-hexane equilibrium than in that of the benzene-cyclohexane reaction, as is shown by the slopes of the respective isotherms.

Polymerization. Parks[143] has stated that the well known tendency of the lower olefins to undergo polymerization may be readily explained by means of free energy calculations. One example, that of the dimerization of isobutene, has already been discussed.[144] Another illustration, that of the polymerization of

[143] G. S. Parks, *Ind. Eng. Chem.*, 1933, **25**, 887; *Chem. Abs.*, 1933, **27**, 4473; *Brit. Chem. Abs.* **A**, 1933, 1014.

[144] See Chapter 26.

hexene-1 to dodecene, will now be considered. Parks has employed ΔF°_{298} values of 14,900 and 21,000 cal., respectively, for these two substances[145] and represented the change in ΔF_{298} for this reaction as:

$$2C_6H_{12(l)} = C_{12}H_{24(l)};\ \Delta F^{\circ}_{298} = 21{,}000 - 2(14{,}900) = -8{,}800 \text{ cal.}$$

From this large negative free energy, Parks concluded that the liquid phase polymerization of an olefin, such as hexene-1, should be virtually complete,[146] even at 25°C.

Production of Isooctane. Vast interest has been shown in the synthetic production of isooctane (2,2,4-trimethylpentane), due to the antiknock properties of this hydrocarbon as a motor fuel.[147] Parks and Todd[148] have investigated the thermodynamic considerations involved in the preparation of this hydrocarbon from isobutene and suggest two mechanisms, both of which will now be discussed.

The first method for producing isooctane involves the polymerization of isobutene to diisobutylene and subsequent hydrogenation to isooctane. For the first step, the change in free energy is given as:

$$(20)\quad 2C_4H_{8(g)} = C_8H_{16(l)};\ \Delta F^{\circ}_{298} = -6{,}930 \text{ cal.}$$

and for the second step:

$$(21)\quad C_8H_{16(l)} + H_{2(g)} = C_8H_{18(l)};\ \Delta F^{\circ}_{298} = -20{,}280 \text{ cal.}$$

Thus, even at 25°C. the rather large negative values of ΔF°_{298} indicate that thermodynamically the reactions may be expected to proceed quite spontaneously and completely from left to right. Parks and Todd allege that these two reactions may be carried out readily even at room temperatures with the proper choice of catalysts. Assuming approximate linear relations for the change in free energy with temperature (that is, taking $\Delta C_p = 0$) equation (20) results in

$$(20a)\quad \Delta F^{\circ}_T = -26{,}770 + 66.6T$$

and equation (21) in

$$(21a)\quad \Delta F^{\circ}_T = -28{,}470 + 27.5T$$

The latter equations show that the free energy will be negative below 402°K. (129°C.) and 1035°K. (762°C.), respectively, both of which are above the boiling points of diisobutylene (101°C.) and isooctane (99°C. for 2,2,4-trimethylpentane).

Considering now the production of both diisobutylene and isooctane in the gaseous phase, the equations become:

$$(20b)\quad \Delta F^{\circ}_T = -17{,}920 + 42.2T$$

from which $\Delta F^{\circ} = 0$ at 425°K. (152°C.) and

$$(21b)\quad \Delta F^{\circ}_T = -28{,}570 + 26.7T$$

from which $\Delta F^{\circ} = 0$ at 1035°K. (762°C.). By the use of moderate pressures (up to 10 atmospheres) of isobutene, Parks and Todd believe that the production of gaseous diisobutylene should be perfectly feasible up to about 200°C.

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[145] Estimations of the free energies of these substances may be made from the general equations for the free energy of formation of olefins [equation (11)] by substituting $T = 298$ and $n = 6$ and 12, respectively. An alternative method would be to use the general equation for the free energy of formation of paraffins [equation (10)] and add on 20,000 cal., for the effect of the double bond, as given in Table 243.

[146] See Chapter 26, this text.

[147] See, for example, Chapters 3, 26 and 44 of this text.

[148] G. S. Parks and S. S. Todd, *Ind. Eng. Chem.*, 1936, **28**, 418; *J. Inst. Pet. Tech.*, 1936, **22**, 253A; *Chem. Abs.*, 1936, **30**, 3401; *Brit. Chem. Abs.* **A**, 1936, 701.

The second method of producing isooctane outlined by Parks and Todd[149] involves the union of isobutene and isobutane, according to the equation:

$$(22)\quad C_4H_{10(g)} + C_4H_{8(g)} = C_8H_{18(l)};\ \Delta F^\circ_{298} = -8{,}250 \text{ cal.}$$

The approximate general equation for the change in free energy as a function of the temperature is:

$$(22a)\quad \Delta F^\circ_T = -27{,}100 + 63.2T$$

from which ΔF° is negative up to 429°K. (156°C.). However, the corresponding equation for the production of gaseous isooctane is

$$(22b)\quad \Delta F^\circ_T = -18{,}350 + 39.1T$$

which gives negative values for the free energy up to 469°K. (196°C.). Parks and Todd state that the latter reaction is not feasible with moderate pressures of isobutane and isobutene at temperatures in excess of 225°C. At this temperature $\Delta F^\circ_{498} = 1{,}130$ cal. and K_p is 0.3, corresponding to about a 6.7 mole per cent concentration of isooctane in equilibrium with 7 atmospheres of isobutane and 7 atmospheres of isobutene.

Parks and Todd assert that the relatively low temperatures required by the above thermodynamic considerations, together with the low reaction velocity and chemical inertness associated with the paraffin hydrocarbons, tend to make reaction (22) appear rather dubious. However, these authorities point out the fact that this type of reaction[150] (especially one involving a tertiary carbon atom, as isobutane) may be made to proceed by means of special catalysts, and cite as an example the work of Ipatieff and Grosse.[151] The latter investigators studied reaction (22) using a catalyst of powdered nickel, boron trifluoride and water, at 25°C., and obtained a 32 per cent yield of octanes. Likewise, experimentally the upper temperature limit of this reaction was found to be about 200°C., which is in essential agreement with the predictions of thermodynamics.

Isomerization. The conversion of cyclohexane into methylcyclopentane may be cited as an example of isomerization. Parks[152] has calculated the free energy change for this transformation in the liquid phase at 25°C. to be:

$$C_6H_{12(l)} = C_5H_9CH_{3(l)};\ \Delta F^\circ_{298} = -4{,}100 \text{ cal.}$$

However, due to the low reactivity of these two hydrocarbons at ordinary temperatures, equilibrium could not probably be reached within reasonable time limits. From Table 241 the change in heat content for this reaction may be calculated as

$$(-37{,}800) - (-36{,}700) = -1{,}100 \text{ cal.}$$

and assuming the change in molal heat capacities of the two hydrocarbons are equal, the approximate equation

$$\Delta F^\circ_T = -1{,}100 - 10T$$

is obtained. Although this equation was based on the liquid phase reaction, according to Parks, it can be applied as a rough approximation to the gaseous phase conversion, since the boiling points and consequently the free energies and heats of vaporization of cyclohexane and methylcyclopentane do not differ very greatly. Thus, at 773°K. (500°C.) the free energy for the gaseous reaction is

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[149] G. S. Parks and S. S. Todd, *loc. cit.*

[150] See Chapter 24.

[151] V. N. Ipatieff and A. V. Grosse, *J.A.C.S.*, 1935, **57**, 1616; *Brit. Chem. Abs.* **A**, 1935, 1348; *Chem. Abs.*, 1935, **29**, 7270.

[152] G. S. Parks, *Ind. Eng. Chem.*, 1933, **25**, 887; *J. Inst. Pet. Tech.*, 1933, **19**, 412A; *Chem. Abs.*, 1933, **27**, 4473; *Brit. Chem. Abs.* **A**, 1933, 1014.

—8,800 cal. In this respect, it is of interest to note that numerous investigators have identified methylcyclopentane among the products obtained in the catalytic reactions of cyclohexane. For instance, Aschan[153] reported that by heating the latter hydrocarbon with fuming hydriodic acid at 300°C., it was converted into methylcyclopentane. Anhydrous aluminum chloride was found not to effect the transformation, as was subsequently verified by Nenitzescu and Cantuniari.[154] These latter investigators, however, observed that by adding traces of water to the aluminum chloride catalyst, yields of as high as 20 per cent of methylcyclopentane could be obtained by heating cyclohexane for 3 hours at about 80°C. Ipatieff and Komarewsky[155] also reported a pronounced conversion to methylcyclopentane with a mixed catalyst of gaseous hydrogen chloride and aluminum chloride.

Hydration of Ethylene. The free energy change involved in the production of ethyl alcohol from ethylene[156] has been the subject of much discussion. Considerable discrepancy exists between the calculations based upon the existing thermodynamic data and those derived from experimental observations, as pointed out by Gilliland, Gunness and Bowles.[157]

These investigators studied the reaction

$$C_2H_{4(g)} + H_2O_{(g)} = C_2H_5OH_{(g)}$$

over a range of temperatures of 175 to 310°C. and pressures of 82.6 to 264.2 atmospheres, using dilute sulphuric acid as a catalyst. From equilibrium data obtained in these experiments, the free energy for the reaction was calculated by means of the equation:

$$\Delta F_T^\circ = -RT \ln \frac{(yf)_{C_2H_5OH}}{(yf)_{C_2H_4}\,(yf)_{H_2O}}$$

where y is the mole fraction of the substance in the vapor phase and f is the fugacity in atmospheres of the pure gas at the temperature in question and at a pressure equal to the total pressure, R is the gas constant and T is the absolute temperature.[158] It was also found that the change in free energy with temperature for this reaction could be expressed by the approximate relation:

$$\Delta F_T^\circ = -7{,}780 + 26.2T$$

This equation correlates well with the experimental work of Sanders and Dodge,[159] Bowles,[160] and Stanley, Youell and Dymock[161] but does not agree with the values of Francis and Kleinschmidt[162] and Parks and Huffman,[163] both of which were based on thermal computations. However, Gilliland, Gunness and Bowles point out that the ΔF°_{298} value of Francis and Kleinschmidt is in good agreement with that obtained by extrapolation of the experimental values, while that of Parks and Huffman is not.[164]

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[153] O. Aschan, *Ann.*, 1902, **324**, 1; *J.C.S.*, 1902, **82** (1), 749; *Chem. Zentr.*, 1902, **2**, 895.

[154] C. D. Nenitzescu and I. P. Cantuniari, *Ber.*, 1933, **66**, 1097; *Ann.*, 1934, **510**, 269; *Chem. Abs.*, 1933, **27**, 4780; 1934, **28**, 5413; *Brit. Chem. Abs.* **A**, 1933, 941; 1934, 773. See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**, Chapter 6. See also Chapter 6, this text.

[155] V. N. Ipatieff and V. I. Komarewsky, *J.A.C.S.*, 1934, **56**, 1926; *Brit. Chem. Abs.* **A**, 1934, 1209; *Chem. Abs.*, 1934, **28**, 6704; *J. Inst. Pet. Tech.*, 1934, **20**, 566A.

[156] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**, Chapter 11. See also Chapter 11, this text.

[157] E. R. Gilliland, R. C. Gunness and V. O. Bowles, *Ind. Eng. Chem.*, 1936, **28**, 380; *Chem. Abs.*, 1936, **30**, 3307; *Brit. Chem. Abs.* **A**, 1936, 565.

[158] According to these authorities, the use of pressures in place of fugacities produces relatively small errors in the free energy values (for instance, at 200 atmospheres, the difference amounts to about 10 per cent). This may be explained by the fact that ethylene acts like an ideal gas under these conditions, and that the deviations of ethanol and water from ideality tend to cancel, since they occur in the free energy equation as a ratio.

[159] F. J. Sanders and B. F. Dodge, *Ind. Eng. Chem.*, 1934, **26**, 208; *J. Inst. Pet. Tech.*, 1934, **20**, 168A; *Chem. Abs.*, 1934, **28**, 2171; *Brit. Chem. Abs.* **B**, 1934, 233.

[160] V. O. Bowles, S. M. Thesis, Mass. Inst. Tech., **1933**.

[161] H. M. Stanley, J. E. Youell and J. B. Dymock. *J.S.C.I.*, 1934, **53**, 205T; *Brit. Chem. Abs.* **A**, 1934, 233; *Chem. Abs.*, 1934, **28**, 2171; *J. Inst. Pet. Tech.*, 1934, **20**, 488A. This work has been substantiated by R. H. Bliss and B. F. Dodge (*Ind. Eng. Chem.*, 1937, **29**, 19). See also, G. S. Parks, *Ind. Eng. Chem.*, 1937, **29**, 845. B. F. Dodge, *Ind. Eng. Chem.*, 1937, **29**, 846.

[162] A. W. Francis and R. V. Kleinschmidt, *Oil and Gas J.*, 1929, **28** (29), 118; *Amer. Pet. Inst. Bull.*, 1930, **III**, 93; *J. Inst. Pet. Tech.*, 1930, **16**, 3A; *Chem. Abs.*, 1930, **24**, 2369.

[163] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, **1932**.

Gilliland, Gunness and Bowles[165] suggest the equation:

$$\Delta F^\circ = -8{,}300 + 26.9T$$

to correlate all of the experimental data mentioned above on the vapor phase hydration of ethylene. This expression is said to be accurate to within ± 500 cal. It is noteworthy that by using dilute sulphuric acid catalysts, liquid-phase concentrations of ethanol as high as 18 per cent were obtained by these investigators. However, they found that the temperature range for the production of ethanol is limited to 220 to 250°C., as below the first temperature ether is formed, and above the latter temperature, polymerization of ethylene interferes.

Production of Higher Alcohols by Hydration. It is interesting to note the thermodynamic possibilities of the direct hydration of some of the higher olefins to alcohols.[166] Eberz and Lucas[167] have studied the equilibrium between isobutene, water and *ter*-butyl alcohol using a dilute nitric acid catalyst. From calculations of the quilibrium constant for the reaction:

$$C_4H_{8(g)} + H_2O_{(l)} = C_4H_9OH_{(l)}$$

at 25°C. and 35°C., they obtained $\Delta F^\circ_{298} = -1{,}330\ (\pm 20)$ cal. and $\Delta F^\circ_{308} = -946$ cal., respectively. These values show that the production of *ter*-butanol is thermodynamically possible even at ordinary temperatures.

Parks[168] has estimated the free energy change in the hydration of hexene-1 to *sec*-hexyl alcohol for the liquid phase process at 25°C. to be approximately 600 cal.[169] Provided chemical inertness is not too great an obstacle, Parks believes that it may be possible to carry out this hydration even at room temperature. However, for the production of *n*-hexyl alcohol from hexane and water, the accompanying free energy change is about 22,000 cal., so that this reaction is unfeasible.

The Fischer Synthesis (Synthol). The synthesis of higher alcohols from carbon monoxide and hydrogen[170] under high pressure may be taken as an illustration of the use of free energy in substantiating a mechanism proposed for a given reaction. For instance, Frolich and Cryder[171] have stated that it is generally conceded that the high molecular weight products are not formed directly in one step, but are the resultants of a series of several reactions. Methanol is undoubtedly an important intermediate in all of these operations.

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[164] In this respect, it should be noted that the ΔF°_{298} values for ethylene (+12,300 cal.) and for ethyl alcohol (−42,200 cal.) are listed by Parks and Huffman as both being uncertain to the extent of ± 2,000 cal. More recent determinations have shown (see Table 240) that the value for ethylene should have been + 15,820 (± 3000) cal., so that the error in this compound alone was almost equal to that assumed for the total reaction

[165] E. R. Gilliland, R. C. Gunness and V. O. Bowles, *loc. cit.*

[166] See Chapter 11. Also, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, **1934**.

[167] W. F. Eberz and H. J. Lucas, *J.A.C.S.*, 1934, **56**, 1230; *Chem. Abs.*, 1934, **28**, 4371; *Brit. Chem. Abs.* **A**, 1934, 731

[168] G. S. Parks, *Ind. Eng. Chem.*, 1933, **25**, 887; *Chem. Abs.*, 1933, **27**, 4473; *Brit. Chem. Abs.* **A**, 1933, 1014.

[169] This result is based on free energies of formation given by G. S. Parks and H. M. Huffman (*loc.* cit.) and may entail a fortuitous error of ±3000 cal.

[170] For a discussion of the thermodynamics of the Fischer-Tropsch Synthin (Kogasin) process, by which hydrocarbons are produced by the catalytic reduction of carbon monoxide, see Chapter 52.

[171] P. K. Frolich and D. S. Cryder, *Ind. Eng. Chem.*, 1930, **22**, 1051; *Brit. Chem. Abs.* **A**, 1930, 1553; *Chem. Abs.*, 1930, **24**, 5717.

Considering first the production of methanol, Parks and Huffman[172] point out that this substance may be formed by the trimolecular reaction:

$$(23)\quad CO + 2H_2 = CH_3OH_{(g)};\ \Delta F^\circ = -22{,}800 + 55.1T$$

or by the two bimolecular reactions advanced by Frolich and Cryder:

$$(24)\quad CO + H_2 = HCHO_{(g)};\ \Delta F^\circ = -1300 + 26.7T$$

and

$$(25)\quad HCHO_{(g)} + H_2 = CH_3OH_{(g)};\ \Delta F^\circ = -21{,}500 + 28.4T$$

involving the formation of formaldehyde and subsequent reduction to methanol. In Fig. 323 Parks and Huffman have plotted the change in free energy with temperature for these reactions (indicated by (23), (24) and (25), respectively). For reaction (23) the free energy change at 600°K. (327°C.) will be +10,000 cal. for the standard state reaction (assuming methanol to be produced at one atmosphere pressure). But by increasing the partial pressure of the hydrogen and carbon monoxide each to 100 atmospheres, Parks and Huffman calculated that the value of ΔF_{600} will be in the magnitude of −6500 cal. Therefore, under the latter conditions, this trimolecular reaction appears very feasible. Similarly, high pressures

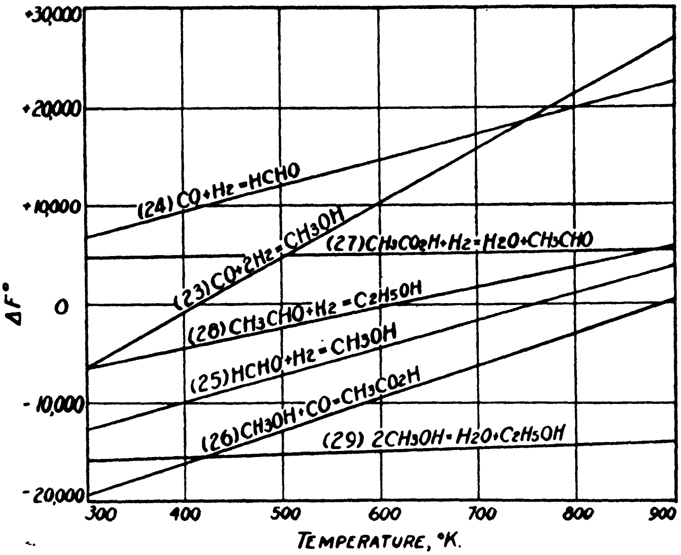

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FIG. 323.—Change in Free Energy with Temperature for Reactions Involved in Synthesis of Alcohols from Carbon Monoxide and Hydrogen. (G. S. Parks and H. M. Huffman)

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[172] G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, 1932, 224. All of the free energy-temperature relations in the present discussion have been calculated by Parks and Huffman. Their equations for methyl alcohol, formaldehyde, ethyl alcohol and acetic acid may be obtained from Table 245. The other approximate equations for the evaluation of change in free energy of formation with temperature that they used are:

$$CO_{(g)}:\ \Delta F^\circ_T = -26{,}500 - 20.7T$$

$$H_2O_{(g)}:\ \Delta F^\circ_T = -58{,}350 + 12.5T$$

and

$$CH_3CHO_{(g)}:\ \Delta F^\circ_T = -43{,}400 + 37.1T$$

are required for the Frolich and Cryder mechanism. Parks and Huffman state that under the above conditions of temperature and pressure equation (24) only becomes feasible if the partial pressure of formaldehyde is kept at about 0.01 atmospheres. However, the partial pressure of the latter substance will depend upon the relative rates[173] of reactions (24) and (25).

According to Fischer[174] the production of higher alcohols may be represented by a series of equations involving primarily the combination of carbon monoxide and methanol to form acetic acid, and the subsequent reduction of this compound to acetaldehyde and finally to ethanol. Using Parks and Huffman's equations for the free energy change with temperature gives:

$$(26)\ CH_3OH_{(g)} + CO = CH_3COOH_{(g)};\ \Delta F^\circ = -29{,}500 + 33.4T$$
$$(27)\ CH_3COOH_{(g)} + H_2 = H_2O + CH_3CHO_{(g)};\ \Delta F^\circ = 3550 + 3.1T$$
$$(28)\ CH_3CHO_{(g)} + H_2 = C_2H_5OH_{(g)};\ \Delta F^\circ = -13{,}600 + 22.1T$$

However, on the basis of experimental observations, Frolich and Cryder disagreed with the mechanism proposed by Fischer and advanced the possibility of a reaction involving the dehydration of two molecules of methanol to form one of ethyl alcohol, as for instance:

$$(29)\ 2CH_3OH_{(g)} = H_2O_{(g)} + C_2H_5OH_{(g)};\ \Delta F^\circ = -16{,}750 + 3.5T$$

Referring again to Fig. 323 it will be seen that the mechanism of Frolich and Cryder is consistent with thermodynamic considerations over the entire temperature range, having a fairly constant value of —13,000 cal. This indicates a large driving force for the dehydration reaction. The equations of Fischer, however, involve reaction (27) for the reduction of acetic acid to acetaldehyde, for which the free energy change is approximately 5000 cal. Offhand, it might therefore be concluded that the Fischer mechanism is incorrect, since one of the standard state reactions involved is thermodynamically unfeasible. However, Parks and Huffman have calculated that at 600°K. (327°C.), with partial pressures of acetic acid vapor, hydrogen, water vapor and acetaldehyde of 1.0, 200, 1.0 and 0.1 atmospheres, respectively, $\Delta F_{600} = -3700$ cal. Thus, although from the theoretical equations this reaction appeared to be very doubtful, under actual operating conditions it may very likely proceed. Parks and Huffman conclude, however, that the mechanism of Frolich and Cryder is undoubtedly the more feasible for explaining this synthesis.

From the above considerations, it will be seen that corrections are often necessary to allow for actual operating conditions. Thus reaction (23) had a standard state free energy (ΔF°_{600}) of +10,000 cal. at 600°K. (327°C.), but under actual operating conditions with high pressures of carbon monoxide and hydrogen, the actual free energy is much different (in the case cited, $\Delta F_{600} = -6500$ cal.). However, when the standard state free energy for a transformation is in the magnitude of +20,000 to 30,000 cal. or more, Parks and Huffman state that the reaction is thermodynamically untenable.[175]

ENGINEERING THERMODYNAMICS

The first portion of this chapter has been devoted to a discussion of thermodynamics as relating to chemical transformations. However, another phase of this science, that dealing with physical changes in a system, is important in engineering calculations. Therefore, the remainder of this chapter will be devoted to a summary of the data available for this branch of thermodynamics directly applicable to petroleum problems and to methods of empirically estimating such data in the absence of experimental values.

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[173] Thus, if the speed of reaction (25) is sufficient to allow no accumulation of formaldehyde, the above partial pressure may result.

[174] F. Fischer, "The Conversion of Coal into Oils," translated by R. Lessing, D. Van Nostrand Co., New York, 1925.

[175] From the above discussion it should be noted that a certain compound may often be produced by more than one reaction, theoretically, at least, in a complex system. Although it may be thermodynamically impossible to account for the presence of this substance by one reaction, another equation or series of equations may be postulated which can explain the apparent discrepancy. This is one of the difficulties at present inherent in petroleum thermodynamics.

The thermodynamic variables most generally employed in engineering calculations, together with their symbols and units, are listed in Table 248.

TABLE 248.—*Thermodynamic Variables for Engineering Calculations.*

		Units	
	Symbol	British System	Metric System
Pressure	P	lbs. per sq. in.	kg. per sq./cm.
Temperature	T	°R. (Rankine, °R. = °F. + 460)	°K. (Kelvin, °K. = °C. + 273)
Volume	V	cu. ft.	liters
Heat Capacity (constant pressure)	C_p	B.t.u. per lb. per °R. (or °F.)	cal. per gram per °K. (or °C.)
Heat Content	H	B.t.u.	cal.
Entropy	S	B.t.u. per °R. (or °F.)	cal. per °K. (or °C.)

The first three of the above variables, pressure, temperature and volume, are in very common usage. They are related by the equation of state, for instance, in the case of an ideal gas, $PV = NRT$, where N is the number of moles and R is the gas constant. The remaining properties, heat capacity, heat content and entropy, are essential in evaluating energy transformations, and merit some further discussion

The heat capacity (or specific heat) may be regarded as the quantity of heat that is required to raise the temperature of one unit of the material under consideration one degree (using consistent units). The heat content, or total heat or enthalpy, as it is sometimes called, is a very useful quantity, since changes in this property indicate directly the quantity of heat gained or lost by a system of constant mass undergoing a transformation at constant pressure. On the other hand, the entropy indicates how any variation in a system affects the ability of that system to do useful work, since the entropy is a measure of the waste thermal energy.

The mathematical relations between Cp, H and S can be best seen from the fundamental partial differential equations:[176]

$$(28)\ C_p = \left[\frac{\delta H}{\delta T}\right]_p \quad \text{and} \quad (29)\ \frac{C_p}{T} = \left[\frac{\delta S}{\delta T}\right]_p$$

Equation (28) may be expressed in words as: the heat capacity at constant pressure is equal to the rate of change of heat content with respect to temperature at constant pressure. Similarly, equation (29) may be stated as the heat capacity at constant pressure, divided by the absolute temperature is equal to the rate of change of entropy with respect to temperature at constant pressure. Under isobaric conditions, therefore, the integrated forms of the above expressions become:

$$(28a)\ dH = \int C_p dT \quad \text{and} \quad (29a)\ dS = \int \frac{C_p dT}{T}$$

respectively.

In general, these thermodynamic properties may be tabulated for each hydrocarbon, not unlike the "steam tables" for the case of water. However, as Lacey and Sage[177] have stated, the graphical representation of these quantities is distinctly advantageous and convenient. For instance, in a simple chart plotted between the temperature as ordinate and the entropy as abscissa, lines of constant pressure, constant volume and constant heat content may be drawn, thus including the complete data for one substance on a single chart.[178]

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[176] Space does not permit a complete discussion of the numerous thermodynamic equations and relations existing between all these variables. Consult G. N. Lewis and M. Randall. "Thermodynamics," McGraw-Hill Book Co., Inc., New York and London, 1923. J. H. Perry, "Chemical Engineers' Handbook," McGraw-Hill Book Co., Inc., New York and London, 1934. The fundamental principles may be found in most elementary volumes on thermodynamics.

Before entering upon a discussion of the charts of this nature and their use it is advisable to review some of the empirical relations that have been developed and may be used in estimating thermodynamic properties both of pure hydrocarbons and mixtures (for instance, petroleum fractions) in the absence of experimental data.

One empirical constant, the Universal Oil Products characterization factor, K (usually referred to as the U.O.P. characterization) has been found to have quite a broad applicability for estimating and correlating various physical and thermal properties of petroleum fractions. In light of this, a brief discussion of this constant is in order.

THE U.O.P. CHARACTERIZATION FACTOR

From data on the physical properties of pure hydrocarbons, Watson and Nelson[179] have observed that the ratio of the cube root of the absolute boiling point to the specific gravity is substantially a constant for the paraffin hydrocarbons boiling between 100 and 700°F. When the boiling point is expressed in degrees Rankine (Fahrenheit, absolute) and the specific gravity at 60°F. referred to water at the same temperature, this ratio varies between 12.5 and 12.8 for paraffin hydrocarbons, whereas for aromatics, the value is 9.8. The definition of the U.O.P. characterization factor arose from the above observations. For narrow-boiling fractions of a crude oil which contains predominantly hydrocarbons of one type, the cube root of the "molal average boiling point" is approximately proportional to the specific gravity of the fraction or:

$$(30)\quad K = \frac{\sqrt[3]{T_B}}{s}$$

where K is the U.O.P. characterization factor, T_B is the molal average boiling point in degrees Rankine (°R = °F. + 460), and s is the specific gravity at 60/60°F.[180] For narrow boiling fractions, the Engler 50 per cent point may be taken as the average boiling point.[181] However, when mixtures of wide boiling range are used, a special method for estimating this quantity must be employed, as will be discussed shortly.

According to Watson and Nelson, the characterization factor denotes what may be termed the "paraffinicity" of the hydrocarbon fraction. Thus, stocks predominantly paraffinic in nature are represented by a factor of 12.5 or thereabout. Fractions that are highly aromatic or naphthenic have a considerably lower characterization, approaching a value of 10 as a minimum. Egloff and Nelson[182] have listed the following values of characterization factors for typical petroleum stocks:

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[177] W. N. Lacey and B. H. Sage, *Oil and Gas J.*, 1934, **33** (26), 86; *Chem. Abs.*, 1935, **29**, 585; *J. Inst. Pet. Tech.*, 1935, **21**, 122A.

[178] Lines of constant values are given special designations on these charts. For instance, lines of constant temperature are known as isotherms, lines of constant volume are isochores and of constant pressure, isobars.

[179] K. M. Watson and E. F. Nelson, *Ind. Eng. Chem.*, 1933, **25**, 880; *Chem. Abs.*, 1933, **27**, 5522; *Brit. Chem. Abs.* **B**, 1933, 995; *J. Inst. Pet. Tech.*, 1933, **19**, 408A.

[180] The symbol 60/60°F. is often used, and signifies that density of the material in question has been measured at 60°F. and is referred to water also at 60°F.

[181] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. See also Chapter 50, this text.

[182] G. Egloff and E. F. Nelson, *Oil and Gas J.*, 1936, **35** (7), 34; *Chem. Abs.*, 1936, **30**, 7828. Also "The Modern Cracking Process," Universal Oil Products Co., Chicago, **1936**.

Pennsylvania stocks	12.2-12.5
Mid-Continent stocks	11.8-12.0
Gulf Coast stocks	11.0-11.5
Cracked gasoline	11.5-11.8
Cracking Plant combined feeds	10.5-11.5
Recycle stocks	10.0-11.0
Cracked residuums	9.8-11.0

Estimation of Average Boiling Point. Watson and Nelson[183] have pointed out that there are several different methods for establishing a so-called average boiling point of petroleum hydrocarbons. By calculating an integrated average ordinate of the true boiling point curve, an accurate average boiling point may be obtained, either on a volumetric or a weight basis, depending upon the units on which the distillation curve is plotted.[184] An Engler distillation curve gives a fair approximation to the volumetric average boiling point, with a tendency toward higher values than would result by averaging a volumetric true boiling point curve. These investigators prefer to use the "molal average boiling point."

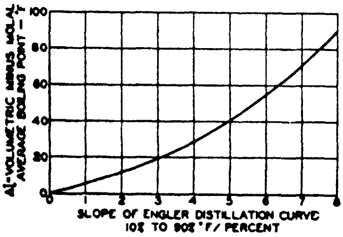

FIG. 324.
Correction Curve for Obtaining Approximate Molal Average Boiling Points. (K. M. Watson and E. F. Nelson)

Courtesy Industrial and Engineering Chemistry

This quantity is less than the volumetric average because of the fact that the ratio of the specific gravity to the molecular weight is higher for the low-boiling members of a hydrocarbon series. Thus, in determining the average boiling point from a volumetric distillation curve, the lower boiling fractions should be given increased weighting in proportion to the variation with boiling point of this ratio of specific gravity to molecular weight, according to Watson and Nelson.

These authorities proposed to obtain an approximation for the molal average boiling point by applying a correction factor to the volumetric average boiling point. This correction factor (see Fig. 324) is expressed as a function of the slope of the 100 cc. Engler distillation curve, and becomes zero as the slope of the curve approaches zero (denoting a pure substance). To obtain the volumetric average boiling point, it is ordinarily sufficient to average the temperatures at which the percentage over plus the distillation loss (in the 100 cc. Engler distillation test) equals 10, 30, 50, 70 and 90 per cent. The slope to be used in Fig. 324 is obtained by dividing the difference between the 90 per cent point and the 10 per cent point by 80. The number of degrees to be subtracted from the volumetric average boiling point is then read from the chart.

When dealing with high-boiling stocks where the temperatures in the distillation exceed 700°F. (which may cause the material to undergo partial cracking), Watson and Nelson prefer to use data from a reduced pressure distillation, correction to atmospheric pressure being made by means of a vapor pressure chart. However, if low-pressure distillation data are not available on these high-temperature stocks, these authorities state that the 50 per cent point probably offers a better approximation to the average boiling point than would that value obtained by averaging the temperatures of the atmospheric distillation curve.

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[183] K. M. Watson and E. F. Nelson, *loc. cit.*
[184] See Chapter 50, this text.

On the basis of later data, Watson, Nelson and Murphy[185] have suggested a more accurate method for approximating the average molal boiling points. For Engler slopes of 3 or less, Fig. 324 is satisfactory. However, where the Engler slope is 8.0, better correlation results when a correction of approximately 60°F. rather than the 90°F. indicated on Fig. 324 is used. Intermediate corrections are similarly reduced. These investigators also state that for close-cut fractions with slopes of 1.5 or less, this correction factor may be neglected and the 50 per cent temperature taken as the average boiling point.

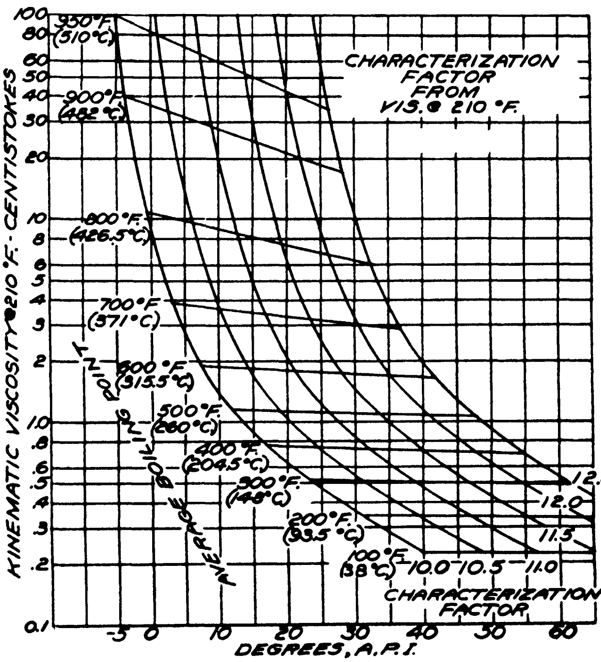

FIG. 325.
Correlation of Characterization Factors, A.P.I. Gravity, Average Boiling Points and Kinematic Viscosity at 210°F. for Petroleum Fractions. (K. M. Watson, E. F. Nelson and G. B. Murphy)

Courtesy Industrial and Engineering Chemistry

ESTIMATION OF THE CHARACTERIZATION FACTOR

The U.O.P. characterization factor, *K*, may be calculated by means of equation (30) from a knowledge of the specific gravity and the average boiling point. Watson, Nelson and Murphy have also found that viscosities, aniline points, viscosity indices and hydrogen contents of petroleum fractions could also be used for evaluating this constant. Of these methods, however, that based on the viscosity is the most universal in its application.

Thus, if the kinematic viscosity at 210°F. (in centistokes[186]) and the gravity (in °A.P.I.) of the oil are known, the characterization factor may be obtained by interpolation of the curves given in Fig. 325. Similarly, from the kinematic viscosity at 122°F. or 100°F. and the gravity, K may be read from Figs. 326 and 327, respectively. The lines of constant boiling point plotted in Figs. 325, 326 and 327 are the resultants of a combination of the relationships between the characterization factor from both boiling point and viscosity data. (These lines permit an approximation of the boiling point from only viscosity and gravity data.) Egloff and Nelson[187] have pointed out that the relationship is particularly useful in the case of heavy stocks on which boiling point data can be obtained only under reduced pressure. However, because of the rapid change in viscosity with a slight variation in the gravity of heavy stocks, estimations such as these may be considerably in error, sometimes as high as 50°F. for the heavier residuums.

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[185] K. M. Watson, E. F. Nelson and G. B. Murphy, *Ind. Eng. Chem.*, 1935, 27, 1460; *J. Inst. Pet. Tech.*, 1936, 22, 49A; *Chem. Abs.*, 1936, 30, 3974; *Brit. Chem. Abs.* B, 1936, 132.

[186] See Chapter 50, this text.

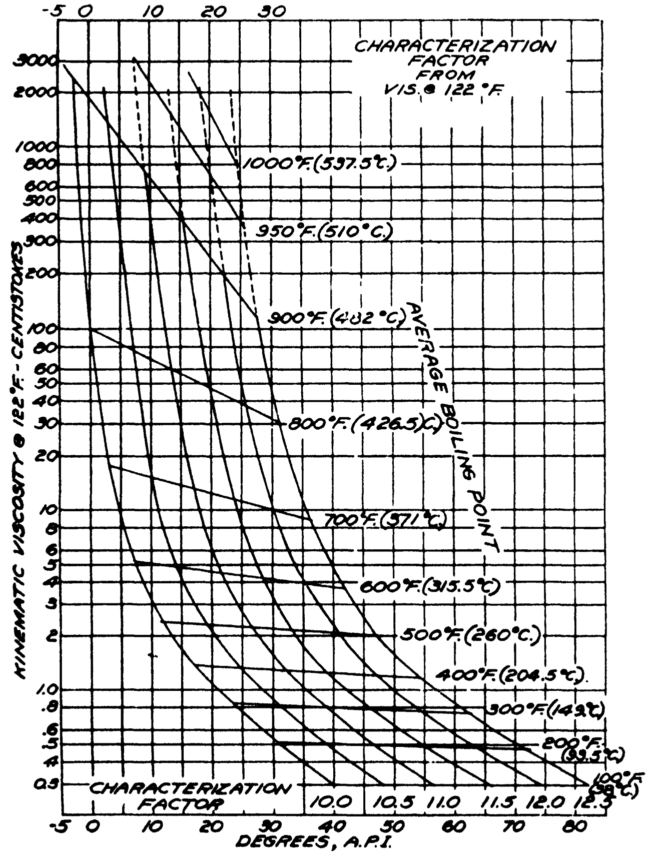

Fig. 326. Chart for Characterization Factors of Petroleum Fractions from A.P.I. Gravity and Kinematic Viscosity at 122°F. (K. M. Watson, E. F. Nelson and G. B. Murphy)

(Courtesy Industrial and Engineering Chemistry)

MOLECULAR WEIGHT OF PETROLEUM FRACTIONS

Watson and Nelson[188] have stated that methods for relating the molecular weight of petroleum fractions to any other single physical property have proved rather unreliable, except for a few limited cases. However, by correlation of two properties, such as specific gravity and boiling point, a relationship can be established which is said to be satisfactory for most purposes. Using the characterization factor and the molal average boiling point, the molecular weight may be obtained with errors less than 5 per cent, according to these investigators, from Fig. 328. Similarly, from the gravity of the oil (in °A.P.I.) and the molal average boiling point, the molecular weight may be estimated from the curves shown in Fig. 329. However, for accurate calculations, Watson and Nelson recommend that an experimental determination of the molecular weight is to be employed whenever possible.

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[187] G. Egloff and E. F. Nelson, *Oil and Gas J.*, 1936, **35** (7), 34; *Chem. Abs.*, 1936, **30**, 7828. Also "The Modern Cracking Process," Universal Oil Products Co., Chicago, **1936**.

[188] K. M. Watson and E. F. Nelson, *Ind. Eng. Chem.*, 1933, **25**, 880; *Chem. Abs.*, 1933, **27**, 5522; *Brit. Chem. Abs.* **B**, 1933, 995; *J. Inst. Pet. Tech.*, 1933. **19**, 408A.

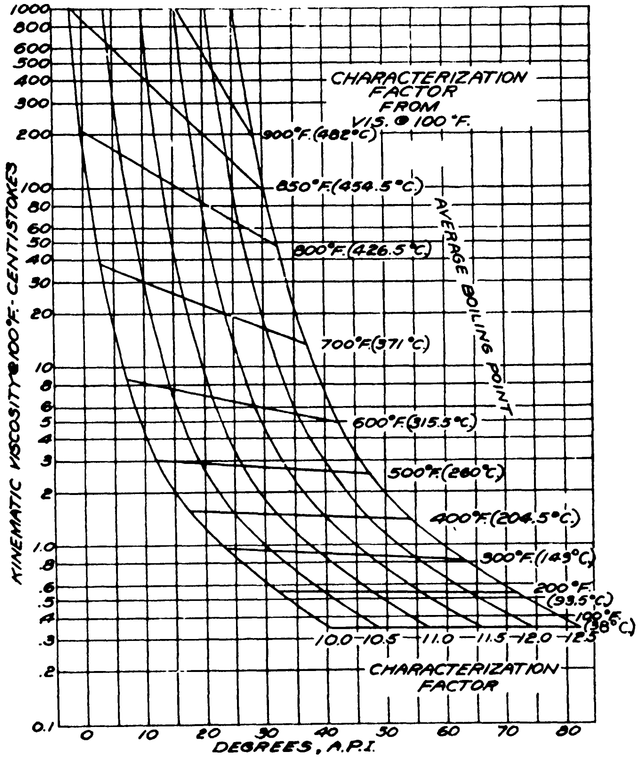


FIG. 327. Characterization Factors of Petroleum Fractions from Kinematic Viscosity at 100°F. and A.P.I. Gravity. (K. M. Watson, E. F. Nelson and G. B. Murphy)

Courtesy Industrial and Engineering Chemistry

ESTIMATION OF THE CRITICAL TEMPERATURE

Eaton and Porter[189] have developed an empirical equation for evaluating the critical temperature of a substance, based on the 50 per cent A.S.T.M. boiling point[190] and the specific gravity. This relation, which was derived from data on both pure hydrocarbons and various petroleum fractions, may be stated as:

$$t_c = 180 + 1.75a - 0.00088a^2$$

[189] G. L. Eaton and C. A. Porter, *Ind. Eng. Chem.*, 1932, **24**, 819; *Brit. Chem. Abs.* **B**, 1932, 825; *Chem. Abs.*, 1932, **26**, 4450.

[190] See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, **1934**. See also Chapter 50 this text.

where $a = (t_b + 100)s$, t_c = critical temperature (°F.), t_b = 50 per cent point (A.S.T.M. distillation) and s = specific gravity at 60°F. Fig. 330 is a graphical representation of this function, by means of which the critical temperature may be determined directly if the 50 per cent point and the specific gravity are known. According to Eaton and Porter, the average deviation in the values of the observed and calculated critical temperatures is about 8°F., although for pure hydrocarbons of higher molecular weight than propane, the average difference is about 5.5°F.

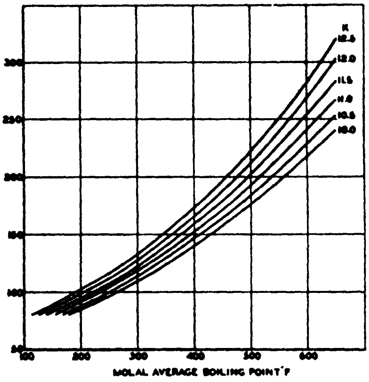


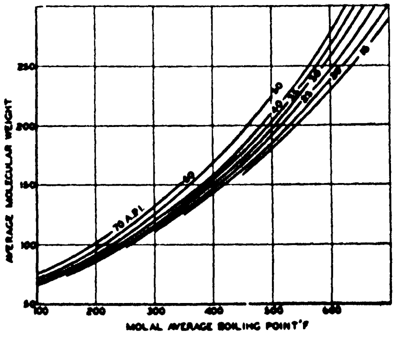
FIG. 328.
Correlation of Characterization Factors and Average Molecular Weights of Petroleum Fractions. (K. M. Watson and E. F. Nelson)

Courtesy Industrial and Engineering Chemistry

Watson and Nelson,[191] however, believe that the use of the molal average boiling point gives a more logical correlation on stocks of wide boiling ranges than does the use of the A.S.T.M. distillation 50 per cent point, as proposed by Eaton and Porter. In Fig. 331 is plotted the relation between the critical temperature (in°F.) and the molal average boiling point for various values of the A.P.I. gravity, as calculated by Watson and Nelson. An illustration of the applicability of this method has been cited by the same workers using the data of Bahlke and Kay[192] for a gasoline and a close-cut naphtha of substantially the same molecular weight and specific gravity. The properties of the two stocks are listed in Table 249.

FIG. 329.
Average Molecular Weights of Petroleum Fractions as Functions of A.P.I. Gravity and Molal Average Boiling Point. (K. M. Watson and E. F. Nelson)

Courtesy Industrial and Engineering Chemistry



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[191] K. M. Watson and E. F. Nelson, *loc. cit.*

[192] W. H. Bahlke and W. B. Kay, *Ind. Eng. Chem.*, 1929, **21**, 942; *Chem. Abs.*, 1930, **24**, 230; *Brit. Chem. Abs.* **B**, 1929, 1004.

TABLE 249.—*Properties of Gasoline and Naphtha of Equal Molecular Weight.*

	Gasoline	Naphtha
Molecular weight (determined)	109	110
Gravity	57.3	57.1
A.S.T.M. distillation curve:		
10%	149	230
30%	230	245
50%	282	258
70%	325	272
90%	371	295
Slope of A.S.T.M. curve	2.8	0.81
Volumetric average b.p.	271	260
Critical temperature (determined)	586	591
Molal average b.p. (from Fig. 324)	254	256

These data show that the gasoline is a lighter stock of lower molecular weight and critical temperature than the naphtha. However, both the 50 per cent point and the volumetric average boiling point are considerably higher than those of the naphtha. When the boiling point is corrected to a molal average basis (by use of Fig. 324) the values of both the average boiling point and the critical temperature fall in the proper order. From Fig. 331 the critical temperatures of these stocks are estimated as 584 and 587°F., respectively.

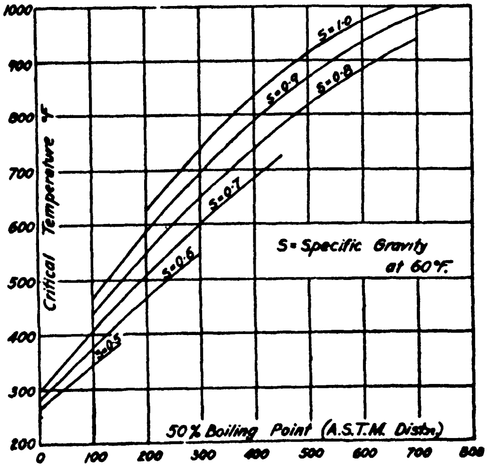

FIG. 330.
Chart for Estimation of Critical Temperatures of Petroleum Fractions from A.S.T.M. 50 Per Cent Boiling Point. (G. L. Eaton and C. A. Porter)

Courtesy Industrial and Engineering Chemistry

The critical temperature may also be estimated in terms of the characterization factor, from the chart prepared by Watson, Nelson and Murphy[193] and given in Fig. 332. This chart may be used to estimate the characterization factor, molecular weight and critical temperature of petroleum fractions from the A.P.I. gravity and the molal average boiling point. Thus, the latter two quantities determine one point on the graph, and by interpolation between the corresponding constant-value lines for characterization factor, molecular weight and critical temperature, the desired property may be approximated.

[193] K. M. Watson, E. F. Nelson and G. B. Murphy, *Ind. Eng. Chem.*, 1935, 27, 1460; *Chem. Abs.*, 1936, 30, 3974.

ESTIMATION OF THE CRITICAL PRESSURE

Determination of the critical pressures of hydrocarbon mixtures is difficult and quite susceptible to large errors unless special precautions are taken. However, Watson and Nelson[194] have proposed a method which offers fair correlation with the available data. This scheme is based on the method of plotting vapor pressure data suggested by Cox[195] for estimating the critical pressure of a pure hydrocarbon whose critical temperature is known. The vapor pressure curves for the pure hydrocarbon when plotted in this manner form straight lines converging at a single point. The critical pressure of a compound whose critical temperature is known may be obtained by drawing a line connecting the normal boiling point of the compound to the point of convergency. The critical pressure is now read from the point of intersection of the vapor pressure curve and the critical temperature abscissa.

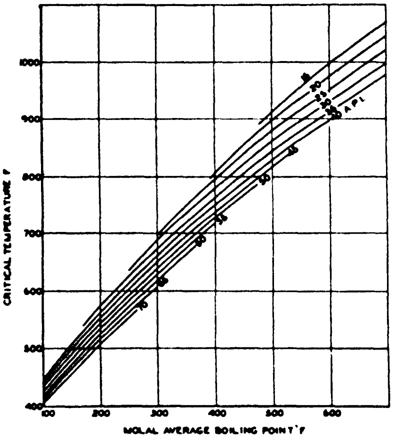

FIG. 331.
Critical Temperatures of Petroleum Fractions from A.P.I. Gravity and Molal Average Boiling Point. (K. M. Watson and E. F. Nelson)

Courtesy Industrial and Engineering Chemistry

Watson and Nelson observed that the average boiling points of mixtures of hydrocarbons usually are approximately straight lines on the Cox chart, and, furthermore, that these lines have the same point of convergency as the pure hydrocarbons. Similarly, the curves representing conditions of initial equilibrium vaporization also are straight lines on the Cox chart, provided the stocks do not contain large quantities of dissolved gases. The investigators point out that the slope of the initial vaporization curve is considerably less than that of the average boiling point curve, so that these two lines intersect at a point beyond the critical temperature of the fraction. As a fair approximation, they found that the latter point of intersection may be assumed to lie at a point beyond the intersection of the average boiling point line and the critical temperature abscissa by a distance equal to 0.2 times the distance between the latter intersection and the atmospheric average boiling point. The temperature of the initial equilibrium vaporization at atmospheric pressure may be taken as the Engler distillation 10 per cent point, in accordance with the views of Bridgeman, Aldrich and White.[196] These assumptions permit an approximation for the initial vaporization line to be established

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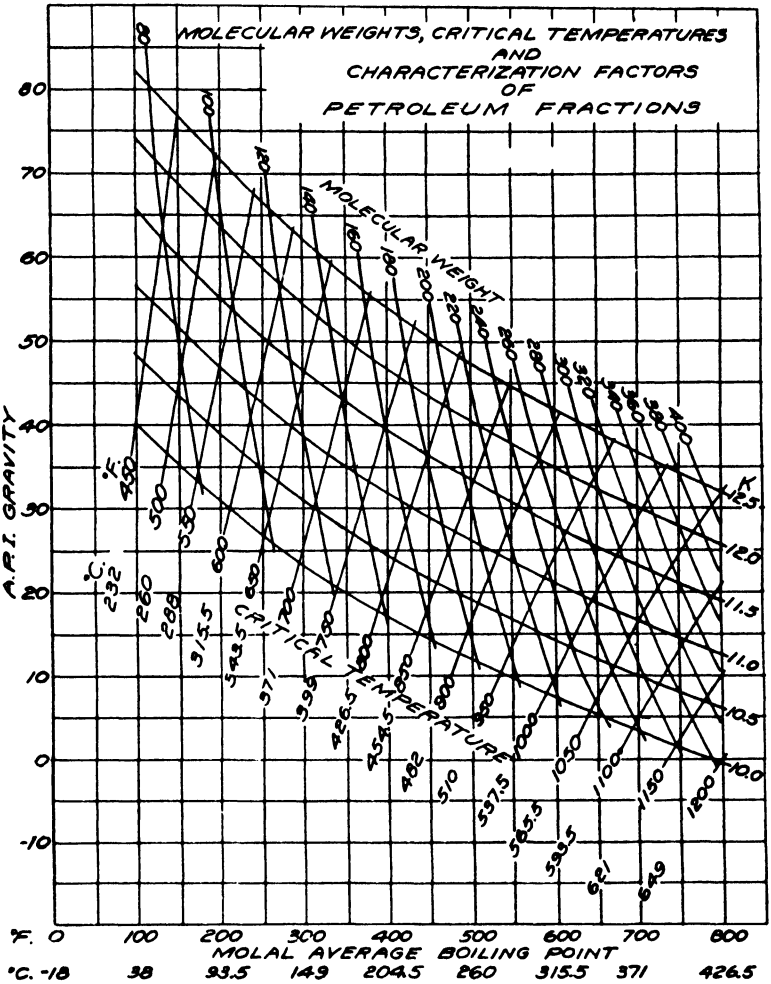
[194] K. M. Watson and E. F. Nelson, *loc. cit.*

[195] E. R. Cox, *Ind. Eng. Chem.*, 1923, 15, 592; *J.S.C.I.*, 1923, 42, 699A; *Chem. Abs.*, 1923, 17, 2359.



Courtesy Industrial and Engineering Chemistry

FIG. 332.—Diagram Correlating Molecular Weights, Critical Temperatures and Characterization Factors of Petroleum Fractions. (K. M. Watson, E. F. Nelson and G. B. Murphy)

on the Cox chart. The critical pressure is then obtained as the pressure corresponding to the intersection of this initial vaporization line with the critical temperature abscissa.

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[196] O. C. Bridgeman, E. N. Aldrich and H. S. White, *Bull. Am. Pet. Inst.*, 1930, 11 (1), 4; *Chem. Abs.*, 1930, 24, 1966.

An illustration of this method has been given by Watson and Nelson,[197] using the data of Weir and Eaton[198] for a naphtha having the following characteristics:

A.P.I. Gravity	58.2
A.S.T.M. Distillation:	
10%	157
30%	211
50%	259
70%	303
90%	353
Volumetric Average B.P.	256
Molal Average B.P. (Predicted from Fig. 324)	241

From Fig. 332, the critical temperature is estimated to be 571°F. The procedure for graphically estimating the critical pressure of this stock is shown in Fig. 333. The series of slanting lines on this chart are the vapor pressure curves for the various paraffin hydrocarbons (the number at the top of the lines refers to the number of carbon atoms in the molecule). The line *FC* is the critical temperature abscissa of this particular naphtha (571°F.). *AB* is the average boiling point line drawn through the atmospheric average boiling point *A* (241°F.) and the point of convergency of the pure hydrocarbon lines. Point *D* is located by measuring along line *AB* a distance of 0.2 times the length of *AC*. Point *E* is the A.S.T.M. 10 per cent point (157°F.). The critical temperature and pressure are represented by point *F*, corresponding to 571°F. and 530 lbs. per sq. in. (absolute). Watson and Nelson point out that these values are in good agreement with the values predicted by Weir and Eaton from the thermal behavior of this distillate, namely 575°F. and 500 lbs. per sq. in.

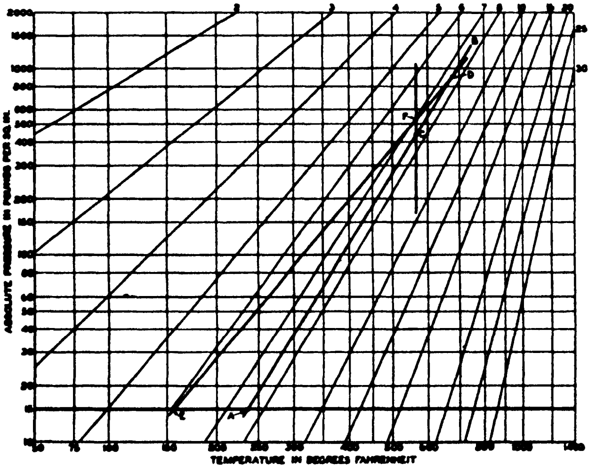

FIG. 333. Chart for Estimating Critical Pressures of Petroleum Fractions. (K. M. Watson and E. F. Nelson)

Courtesy Industrial and Engineering Chemistry

A more accurate method of estimating the critical pressure of hydrocarbon mixtures has been suggested by Egloff and Nelson,[199] based on the vapor pressure

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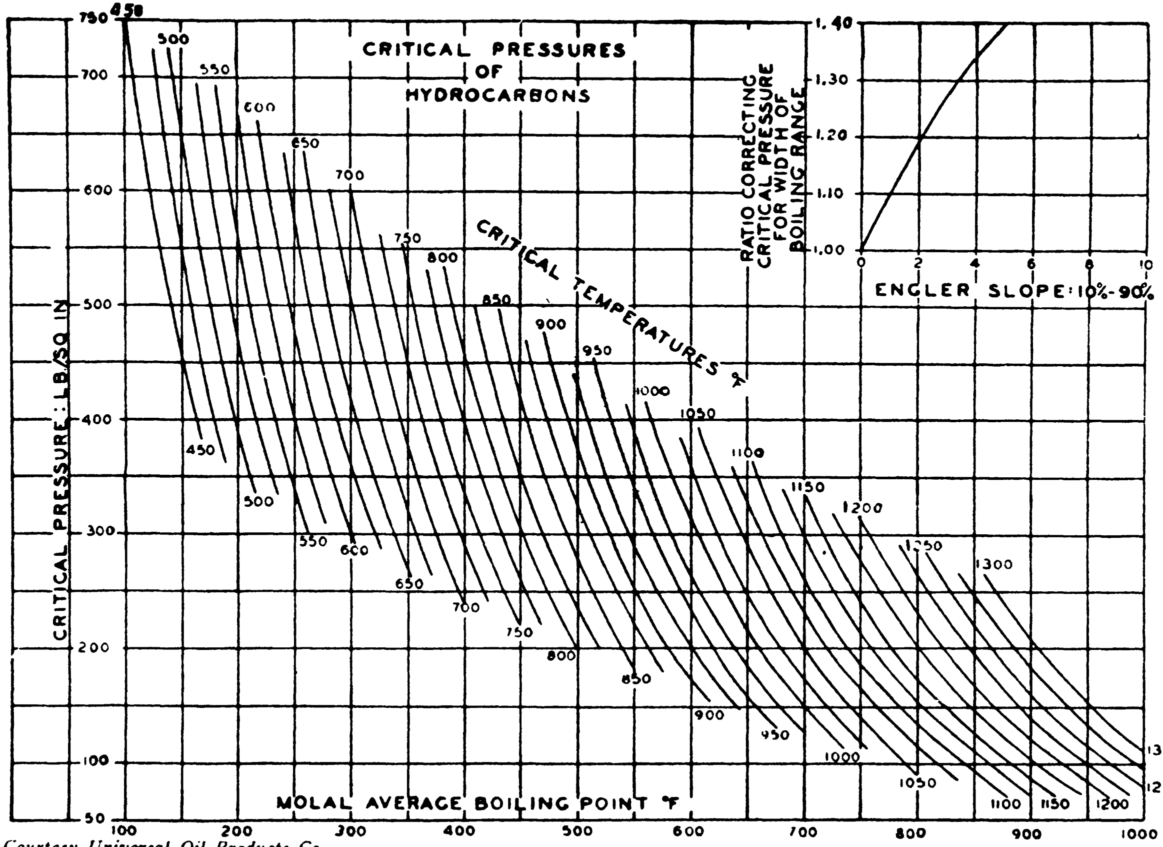
[197] K. M. Watson and E. F. Nelson, *Ind. Eng. Chem.*, 1933, 25, 880; *Chem. Abs.*, 1933, 27, 5522; *Brit. Chem. Abs.* B, 1933, 995; *J. Inst. Pet. Tech.*, 1933, 19, 408A.

[198] H. M. Weir and G. L. Eaton, *Ind. Eng. Chem.*, 1932, 24, 211; *Brit. Chem. Abs.* B, 1932, 327; *Chem. Abs.*, 1932, 26, 1760.

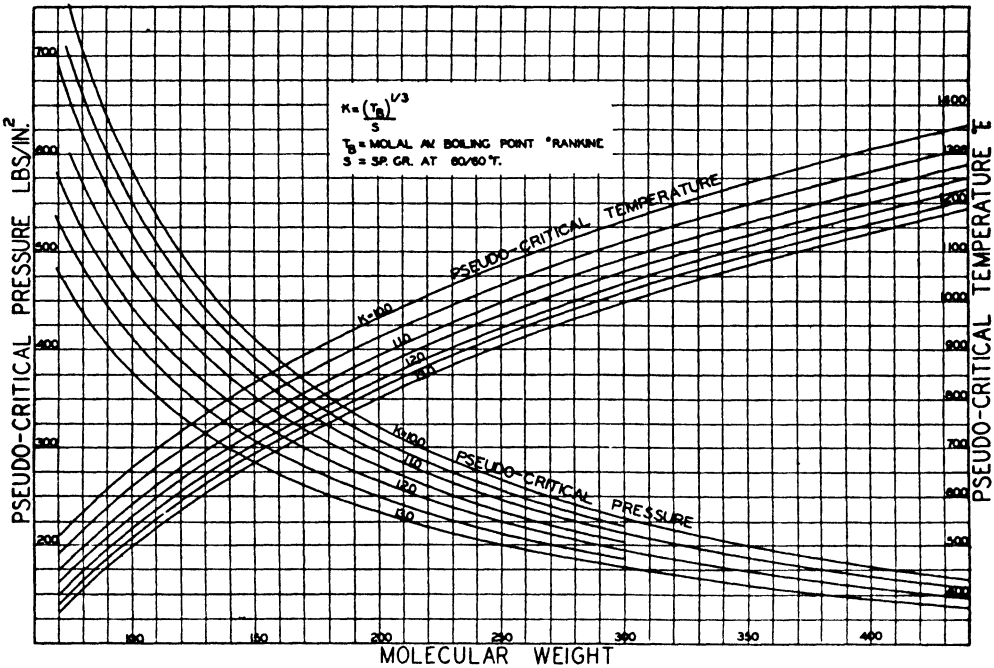
[199] G. Egloff and E. F. Nelson, *Oil and Gas J.*, 1936, 35 (7), 34; *Chem. Abs.*, 1936, 30, 7828. Also "The Modern Cracking Process," Universal Oil Products Co., Chicago, 1936.



Courtesy Universal Oil Products Co.

Fig. 334.—Curves Relating Boiling Points and Critical Pressures of Hydrocarbons. (G. Egloff and E. F. Nelson)

chart of Coats and Brown,[200] and is shown in Fig. 334. From this graph, the critical pressure of the hydrocarbons is determined from the molal average boiling point and the critical temperature. The small curve plotted in the upper corner of this figure shows the correction factor by which the critical pressure of a pure compound is multiplied to obtain the critical pressure of a mixture having the same average boiling point, gravity and critical temperature. This correction factor is related to the slope of the Engler distillation curve in the same manner as that of Fig. 324. The latter method is a convenient means of approximation, and is said to be in fair agreement with the available data.



Courtesy Industrial and Engineering Chemistry

FIG. 335.—Pseudocritical Temperatures and Pressures of Hydrocarbon Mixtures. (W. B. Kay)

Kay[201] has correlated the pseudocritical temperatures and pressures[202] of hydrocarbons in terms of the characterization factor and the molecular weight of the fraction. These relations are given in Fig. 335. According to Kay, the critical values of mixtures composed of lower molecular weight hydrocarbons may be estimated with an error of 2 or 3 per cent. However, in the case of higher molecular weight fractions, the error may be somewhat greater.[203]

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[200] H. B. Coats and G. G. Brown, *Univ. Mich. Dept. Eng. Research, Cir. Series*, 1928, **2**, 1; *Chem. Abs.*, 1929, **23**, 3610; *Brit. Chem. Abs.* **A**, 1929, 387.

[201] W. B. Kay, *Ind. Eng. Chem.*, 1936, **28**, 1014; *Chem. Abs.*, 1936, **30**, 7828; *Brit. Chem. Abs.* **A**, 1936, 1330.

[202] The "pseudocritical point" of a mixture corresponds to the critical point of a pure hydrocarbon of the same physical characteristics (i.e., molecular weight, boiling point and so forth). According to W. B. Kay (*loc. cit*), the pseudocritical point of a mixture has no real existence and therefore cannot be measured. Only for mixtures of very narrow boiling range is it approximately equal to the true critical point.

Pressure-Volume-Temperature Relations of Hydrocarbons

The introduction of high temperature and high pressure developments in the petroleum field has necessitated a knowledge of the properties of the substances under these conditions. Especially in the gaseous or vapor phase are materials sensitive to changes in temperature and pressure, as Lewis[204] has pointed out. The ideal gas laws are exact only at very low pressure, and it was generally recognized that in some instances deviations of from 10 to 20 per cent were not uncommon, even when dealing with pressures of 100 to 200 lbs. per sq. in. However, these errors were seldom as large as other uncertainties in design problems, and therefore, ordinarily, engineers did not hesitate to take advantage of the simplicity of these relations. But in the case of high pressure operations, it was found that these deviations may reach several hundred per cent and as such would have to be considered in calculations.

Reduced Equation of State. The so-called reduced equation of state offers a possible basis for the generalized treatment of gases and vapors. Designating the pressure, volume and temperature of a substance at the critical point as P_c, V_c and T_c, respectively, the values of these quantities under any other conditions may be expressed as a ratio (commonly known as the reduced property) in terms of the critical constants. Thus, the reduced pressure is $P_r = \frac{P}{P_c}$, where P is the pressure and P_c is the critical pressure for the material under consideration. Similarly, the reduced volume may be expressed as $V_r = \frac{V}{V_c}$, and the reduced temperature as $T_r = \frac{T}{T_c}$.

For one mole of a material, regardless of the deviation of the vapor from the ideal gas laws, the equation of state may be written as $PV = \mu RT$, where R is the gas constant and μ is the correction factor to allow for deviation (necessarily a dimensionless ratio).[205] Substituting for the three variables in the above equation their equivalents in terms of the critical and reduced properties gives:

$$\frac{P_r V_r}{T_r} = \frac{\mu R T_c}{P_c V_c}$$

Lewis states that if, for a given group of substances a single reduced equation of state exists (as designated mathematically by the notation $V_r = f\ (P_r,\ T_r)$ where f represents the same function for the entire group), regardless of how complicated this relationship may be, it must reduce to the above form at sufficiently low pressure values. However, the right-hand side of this equation is a constant for a given compound, and so it follows that this constant must be identical for all substances of the group. Thus, Lewis believes that a common reduced equation of state is impossible except for substances having identical critical ratios of

$$\frac{RT_c}{P_c V_c}.$$

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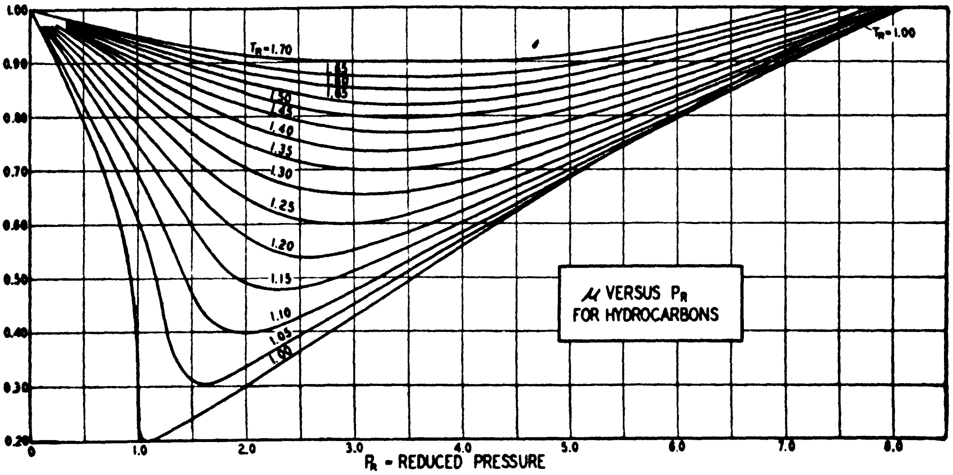
[203] Consult L. C. Roess (*J. Inst. Pet. Tech.*, 1936, **22**, 665; *J. Inst. Pet. Tech.*, 1936, **22**, 539A) for a discussion of the development of a flow method for determining the critical temperature and pressure of petroleum fractions up to 1000° F. and 600 lbs. per sq. in., respectively, and the correlation between these properties and other physical properties which are more readily determined.

[204] W. K. Lewis, *Ind. Eng. Chem.*, 1936, **28**, 257; *Chemistry and Industry*, 1936, 123; *Chem. Abs.*, 1936, **30**, 1893; *J. Inst. Pet. Tech.*, 1936, 22, 146A; *Brit. Chem. Abs.* **B**, 1936, 255.

[205] Thus for an ideal gas, since $\mu = 1$, $PV = RT$. A dimensionless ratio is a pure number, i.e., one which requires no qualifying units.

Correlation of P-V-T Data. A survey of the available data on hydrocarbons by Brown, Lewis and Weber[206] showed that a reduced equation of state was applicable to all compounds of this type above propane. According to Lewis,[207] the experimental data for all hydrocarbons indicates a maximum deviation of about 12 per cent in the critical ratio. However, when the low-boiling compounds of small molecular weight are excluded, this variation does not exceed 3 per cent. Therefore, it is permissible to compare the P-V-T characteristics of hydrocarbons containing more than three carbon atoms on a reduced basis.



Courtesy Industrial and Engineering Chemistry

FIG. 336.—Diagram of P-V-T Relations of Hydrocarbons at Temperatures Above Critical. (W. K. Lewis)

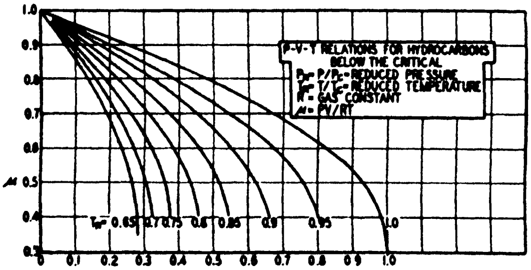


FIG. 337. Correlation of P-V-T Data for Hydrocarbons at Temperatures Below Critical. (W. K. Lewis)

Courtesy Industrial and Engineering Chemistry

The curves in Figs. 336 and 337 have been prepared by Lewis to indicate this correlation for hydrocarbons above and below the critical conditions, respectively. In these graphs, the values of the deviation from ideality, μ, are plotted against the reduced pressure, P_r, for different values of the reduced temperature, T_r. Lewis has emphasized the advantages in the use of these charts for calculating pressure-volume-temperature relations. This type of chart completely eliminates the necessity for knowledge of the critical volume of the specific compound. Thus, if the critical temperature and pressure are available, and the independent variables T and P are known, the reduced properties can be readily calculated. The value

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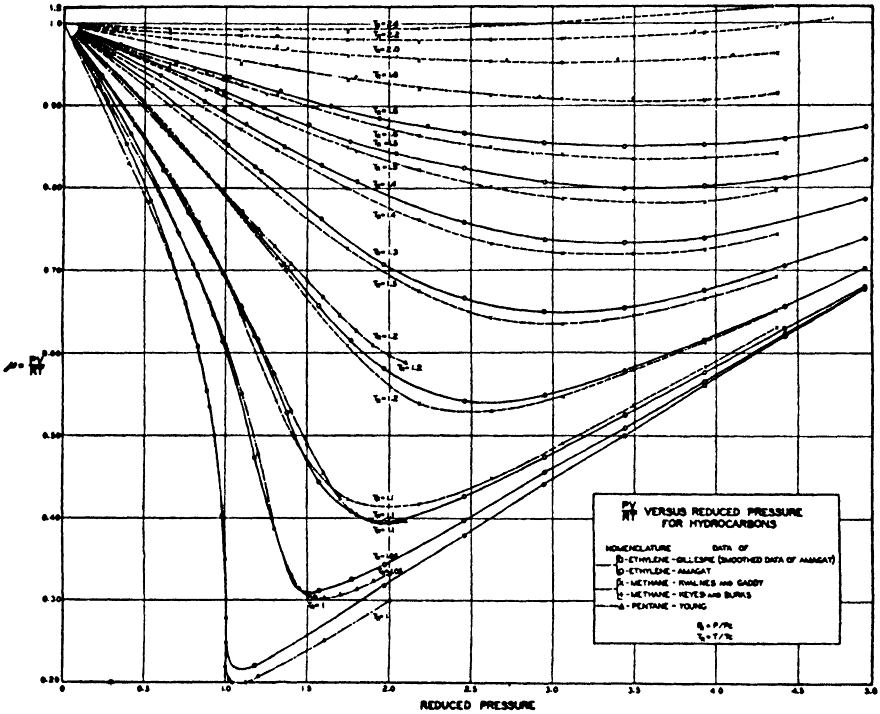
[206] G. G. Brown, W. K. Lewis and H. C. Weber, *Ind. Eng. Chem.*, 1934, **26**, 325; *Brit. Chem. Abs.* **B**, 1934, 486; *Chem. Abs.*, 1934, **28**, 3567.
[207] W. K. Lewis, *loc. cit.*



Courtesy Industrial and Engineering Chemistry

FIG. 338.—Chart of P-V-T Relationships for Methane, Ethylene and Isopentane. (G. G. Brown, W. K. Lewis and H. C. Weber)

of μ may be interpolated from the curves given in Figs. 336 or 337 and substituted in the equation:

$$PV = N\mu RT$$

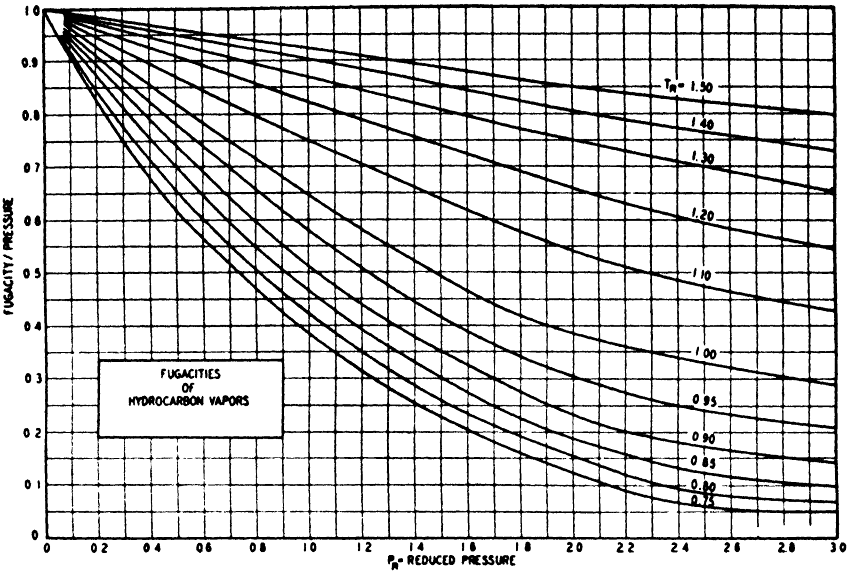
(N is the number of moles) to give V, the volume occupied by the gas under the assumed conditions. It should be noted that μ is a dimensionless ratio and is numerically independent of the units of measurement employed, provided they are consistent. The quantity R is the gas constant and should be expressed in whatever units are employed throughout the equation.

Although these curves were derived for pure hydrocarbons, Lewis[208] has also applied them to steam, carbon dioxide and ammonia vapor, and has concluded that

[208] W. K. Lewis, *Ind. Eng. Chem.*, 1936, **28**, 257; *Chemistry and Industry*, **1936**, 123; *Chem. Abs.*, 1936, **30**, 1893; *J. Inst. Pet. Tech.*, 1936, **22**, 146A; *Brit. Chem. Abs.* **B**, 1936, 255.

these curves can be used with reasonable accuracy to approximate the properties of other compounds, even though widely different in type.

Brown, Lewis and Weber[209] have plotted the available data for methane, ethylene and isopentane, as is shown in Fig. 338. From this figure it will be noted that for the lower temperature isotherms, the latter hydrocarbon gives lower values for μ than methane and ethylene, but that this condition is reversed on the higher reduced temperature curves.[210]



Courtesy Industrial and Engineering Chemistry

FIG. 339.—Ratio of Fugacity to Pressure Plotted Against Reduced Pressure for Various Reduced Temperatures. (W. K. Lewis)

Fugacity. Since the ideal gas laws do not hold at high pressures, similar general relations, such as mass action and liquid-vapor equilibria formulas and other equations involving substances in the vapor state, will also be considerably in error. However, by substituting for the pressure a corrected function of the same dimensions (the so-called fugacity, designated by the symbol f) these equations may still be used.

Lewis[211] has demonstrated that the ratio of the fugacity to the corresponding pressure $\left(\frac{f}{P}\right)$ is a unique function of the reduced temperature and pressure for a group of substances conforming to a single reduced equation of state (as, for instance, the higher hydrocarbons). By graphical integration of Figs. 336 and 337, he obtained a series of curves, as shown in Fig. 339, in which the ratio of $\frac{f}{P}$ is plotted against the reduced pressure for different values of reduced temperature. From the latter chart, the values of the fugacity of any hydrocarbon may be calculated at any pressure, provided the necessary critical constants are available.[212]

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[209] G. G. Brown, W. K. Lewis and H. C. Weber, *Ind. Eng. Chem.*, 1934, **26**, 325; *Brit. Chem. Abs.* **B**, 1934, 486; *Chem. Abs.*, 1934, **28**, 3567.

[210] For other discussions on *P-V-T* relations see also: K. M. Watson and R. L. Smith, *Nat. Pet. News*, 1936, **28** (27), 29; *Chem. Abs.*, 1936, **30**, 6255; *Brit. Chem. Abs.* **A**, 1936, 1331; *J. Inst. Pet. Tech.*, 1936, **22**, 394A. Also "Generalized High Pressure Properties of Gases," Universal Oil Products Co., Chicago, 1936. E. R. Gilliland, *Ind. Eng. Chem.*, 1936, **28**, 212; *J. Inst. Pet. Tech.*, 1936, **22**, 151A; *Brit. Chem. Abs.* **A**, 1936, 419; *Chem. Abs.*, 1936, **30**, 1623. W. B. Kay, *Ind. Eng. Chem.*, 1936, **28**, 1014; *Chem. Abs.*, 1936, **30**, 7828; *Brit. Chem. Abs.* **A**, 1936, 1330; *J. Inst. Pet. Tech.*, 1936, **22**, 539A. W. K. Lewis and C. D. Luke, *Trans. Am. Soc. Mech. Engrs.* (*Petroleum Mech. Eng.*), 1932, **54** (17), 55; *Chem. Abs.*, 1933, **27**, 3495. *Ind. Eng. Chem.*, 1933, **25**, 725; *Brit. Chem. Abs.* **A**, 1933, 895; *Chem. Abs.*, 1933, **27**, 4145.

[211] W. K. Lewis, *loc. cit.*

ESTIMATION OF THERMAL PROPERTIES

The thermal properties of a large number of substances have been determined experimentally. From the data accumulated in this manner, a number of empirical relations have been deduced which may be employed in estimating the thermal data for hydrocarbons in general, or mixtures of hydrocarbons, such as petroleum fractions, in the absence of any available experimental information.

SPECIFIC HEAT

Vapor State. The vapor phase specific heat determinations of Bahlke and Kay,[213] Weir and Eaton,[214] and Gary, Rubin and Ward[215] on the Mid-Continent crude fractions have been found to be in excellent agreement. To establish a basis for estimating the specific heats of vapors of stocks other than those of the above-mentioned type, Watson and Nelson[216] have modified the equation proposed by Bahlke and Kay, by the insertion of a term involving the characterization factor, to give:

$$C_p = \frac{4.0 - s}{6{,}450} (t + 670) (0.12K - 0.41)$$

where C_p is the specific heat of the vapor, t is the temperature (°F.), s is the specific gravity (60/60°F.) and K is the characterization factor. For Mid-Continent stocks ($K = 11.8$) the correction factor reduces to unity. Fig. 340, prepared by Egloff and Nelson,[217] is a graphical representation of the above equation. The specific heats of Mid-Continent stocks and paraffin gases may be read directly from this graph. (For light stocks, the specific gravity is referred to air as 1 and for heavy stocks it is in terms of the A.P.I. gravity of the liquid).[218] For a stock having a characterization other than 11.8, the correction by which the above value is multiplied to give the specific heat is read from the small inset curve.[219]

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[212] For discussions of the use of fugacity in calculating vapor-liquid equilibria in hydrocarbon systems consult: W. K. Lewis, *Ind. Eng. Chem.*, 1936, **28**, 257; *Chemistry and Industry*, **1936**, 123; *Chem. Abs.*, 1936, **30**, 1893; *J. Inst. Pet. Tech.*, 1936, **22**, 146A; *Brit. Chem. Abs.* **B**, 1936, 255. W. K. Lewis and C. D. Luke, *loc. cit.* G. G. Brown, W. K. Lewis and H. C. Weber, *loc. cit.* K. M. Watson and R. L. Smith, *loc. cit.* M. Souders, Jr., C. W. Selheimer and G. G. Brown, *Ind. Eng. Chem.*, 1932, **24**, 517; *Brit. Chem. Abs.* **A**, 1932, 696; *Chem. Abs.*, 1932, **26**, 3416. Also A. I. Krasil'shchikov, *J. Phys. Chem. (U.S.S.R.)*, 1935, **6**, 1362; *Chem. Abs.*, 1937, **31**, 22.

[213] W. H. Bahlke and W. B. Kay, *Ind. Eng. Chem.*, 1929, **21**, 942; *Chem. Abs.*, 1930, **24**, 230; *Brit. Chem. Abs.* **B**, 1929, 1004.

[214] H. M. Weir and G. L. Eaton, *Ind. Eng. Chem.*, 1932, **24**, 211; *Brit. Chem. Abs.* **B**, 1932, *327; Chem. Abs.*, 1932, **26**, 1760.

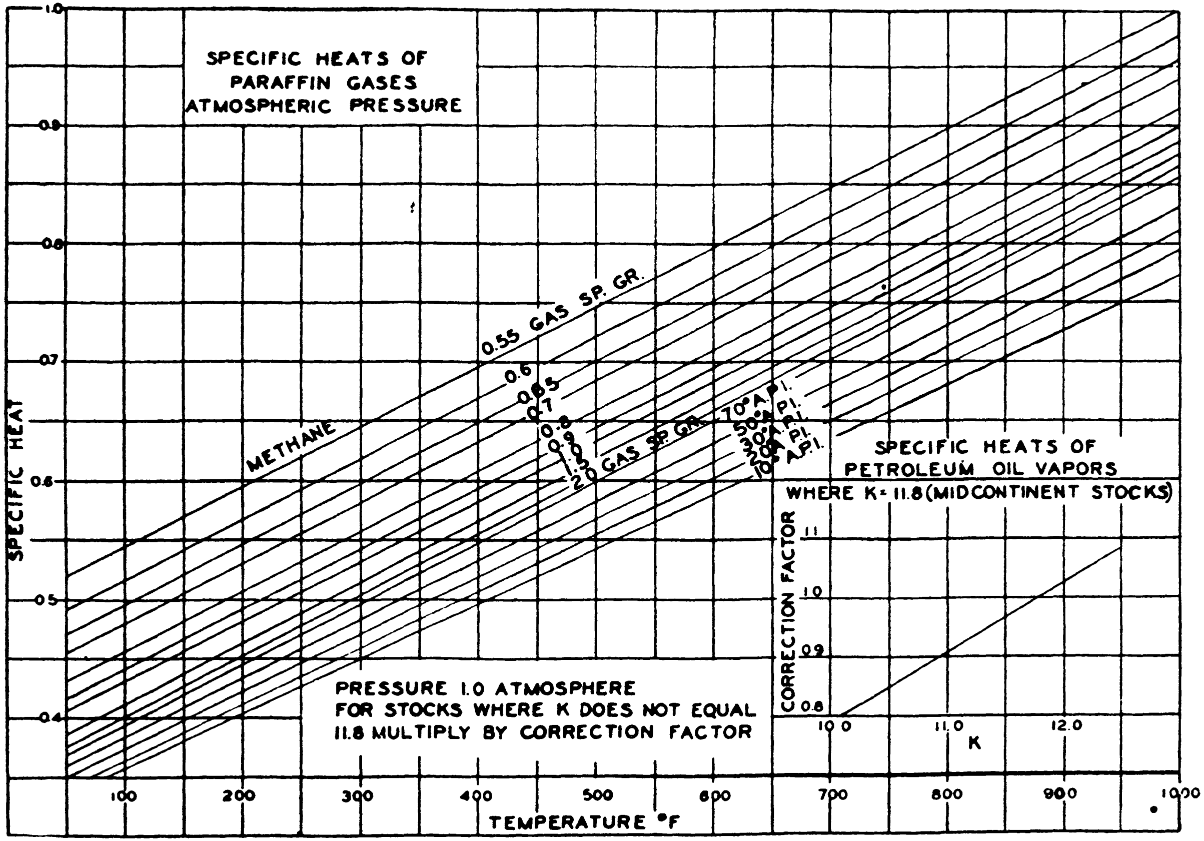
[215] W. W. Gary, L. C. Rubin and J. T. Ward, *Ind. Eng. Chem.*, 1933, **25**, 178; *Brit. Chem. Abs.* **B**, 1933, 293; *Chem. Abs.*, 1933, **27**, 1492.

[216] K. M. Watson and E. F. Nelson, *Ind. Eng. Chem.*, 1933, **25**, 880; *Chem. Abs.*, 1933, **27**, 5522; *Brit. Chem. Abs.* **B**, 1933, 995; *J. Inst. Pet. Tech.*, 1933, **19**, 408A.

[217] G. Egloff and E. F. Nelson, *Oil and Gas J.*, 1936, **35** (7), 34; *Chem. Abs.*, 1936, **30**, 7828. Also "The Modern Cracking Process," Universal Oil Products Co., Chicago, **1936**.

[218] This portion of the plot corresponds to the equation of Bahlke and Kay for Mid-Continent oils.

[219] The heat capacities of a number of the common gases have been revised by E. D. Eastman, "Specific Heats of Gases at High Temperatures," *U. S. Bureau of Mines Tech. Paper 444*, **1929**; *Chem. Abs.*, 1929, **23**, 3610. See A. C. Halferdahl (*Chem. and Met. Eng.*, 1930, **37**, 686; *Brit. Chem. Abs.* **A**, 1931, 156; *Chem. Abs.*, 1931, **25**, 242) for a graphical representation of these data. See also J. H. Perry, "Chemical Engineers' Handbook," McGraw-Hill Book Co., Inc., New York and London, **1934**.



Courtesy Universal Oil Products Co.

FIG. 340.—Chart for Specific Heats of Petroleum Vapors. (G. Egloff and E. F. Nelson)

Liquid State. Gaucher[220] has correlated the available data on the specific heats of pure hydrocarbons in the liquid state by means of the equation:

$$C_p = 0.6230 - 0.0187 \frac{\sqrt{T}}{\sqrt{s^3}} + 0.000355\frac{T}{s^3} + 0.00045(t - 32)$$

or in terms of the characterization factor:

$$C_p = 1.323 - 0.2005K + 0.0107K^2 + 0.00045(t - 32)$$

where T = boiling point, in degrees Rankine (Fahrenheit, absolute), s = specific gravity (60/60°F.), t = temperature (°F.), C_p = specific heat at t°F. and K = the characterization factor $\left(\frac{\sqrt[3]{T}}{s}\right)$. Either of these equations is said to express the specific heat of pure hydrocarbons with an average deviation of 1.3 per cent and a maximum of 6 per cent on the basis of the available experimental data.

According to Gaucher, the specific heats of liquid petroleum fractions are best represented by the relationship proposed by Watson and Nelson,[221]

$$C_p = [0.6811 - 0.308s + t(0.000815 - 0.000306s)]\,[0.055K + 0.35.]$$

The symbols here are the same as given above. Fig. 341 is a graphical representation of this function. Thus, the values for Mid-Continent fractions (K = 11.8) may be estimated directly from the main chart. For other stocks, this number is multiplied by the correction obtained from the characterization factor as indicated in the inset curve to give the specific heat. According to Watson and Nelson, the above equation may cause a considerable error at conditions near the critical state because of the variation of C_p with pressure. However, this relation is said to be applicable to pressures well above that required to prevent vaporization, but may give results much too low at sub-atmospheric pressure.[222]

HEAT OF VAPORIZATION

Of the numerous methods[223] for estimating latent heats, Watson and Nelson[224] have stated that the equation proposed by Kistyakovskii[225] for pure hydrocarbons:

$$L = \frac{T_B}{M}(7.58 + 4.571 \log T_B)$$

where L = latent heat of vaporization (B.t.u. per lb.), T_B = normal boiling point (degrees Rankine, °R = °F + 460) and M = molecular weight, may be used as an approximation for hydrocarbon mixtures, provided the average molecular weight and boiling point are used. Assuming the applicability of the above equa-

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[220] L. P. Gaucher, *Ind. Eng. Chem.*, 1935, **27**, 57; *J. Inst. Pet. Tech.*, 1935, **21**, 85A; *Brit. Chem. Abs.* **A**, 1935, 289; *Chem. Abs.*, 1935, **29**, 1972.

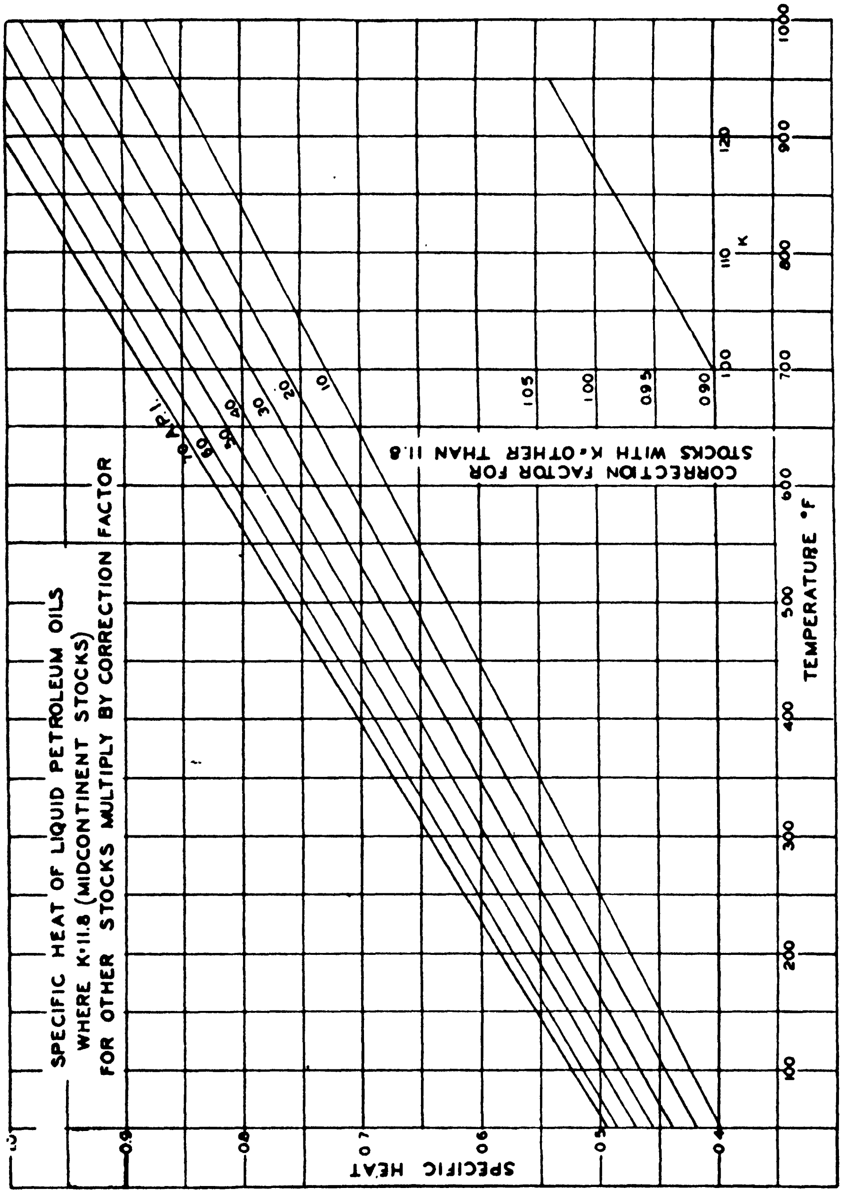
[221] K. M. Watson and E. F. Nelson, *Ind. Eng. Chem.*, 1933, **25**, 880; *Chem. Abs.*, 1933, **27**, 5522; *Brit. Chem. Abs.* **B**, 1933, 995; *J. Inst. Pet. Tech.*, 1933, **19**, 408A.

[222] For other work on specific heats of petroleum fractions see: A. R. Fortsch and W. G. Whitman, *Ind. Eng. Chem.*, 1926, **18**, 795; *Brit. Chem. Abs.* **B**, 1926, 810; *Chem. Abs.*, 1927, **21**, 169. H. M. Weir and G. L. Eaton, *Ind. Eng. Chem.*, 1932, **24**, 211; *Brit. Chem. Abs.* **B**, 1932, 327; *Chem. Abs.*, 1932, **26**, 1760. H. R. Lang and R. Jessel, *J. Inst. Pet. Tech.*, 1930, **16**, 783; 1931, **17**, 572; 1932, **18**, 850; *Brit. Chem. Abs.* **B**, 1931, 143, 1034; 1933, 374; *Chem. Abs.*, 1931, **25**, 2275; 1932, **26**, 584; 1933, **27**, 1741. W. W. Gary, L. C. Rubin and J. T. Ward, *Ind. Eng. Chem.*, 1933, **25**, 178; *Chem. Abs.*, 1933, **27**, 1492; *Brit. Chem. Abs.* **B**, 1933, 293. C. S. Cragoe, *Bur. Standards, Miscellaneous Pub.*, 97, **1929**; *Brit. Chem. Abs.* **B**, 1930, 228; *Chem. Abs.*, 1930, **24**, 1496. A. J. E. Swann, *Fuel*, 1932, 11, 113; *Chem. Abs.*, 1932, **26**, 3654; *Brit. Chem. Abs.* **B**, 1932, 409. W. Goldstern, *Petroleum Z.*, 1936, **32** (36), 1; *Brit. Chem. Abs.* **B**, 1936, 1028.

[223] For the use of Trouten's rule see: C. S. Cragoe, *loc. cit.* H. M. Weir and G. L. Eaton, *loc. cit.* W. W. Gary, L. C. Rubin and J. T. Ward, *loc. cit.* See also J. H. Hildebrand, *J.A.C.S.*, 1915, **37**, 970; *Chem. Abs.*, 1915, **9**, 1423; *J.C.S.*, 1915, **108** (2), 416. W. K. Lewis and H. C. Weber, *Ind. Eng. Chem.*, 1922, **14**, 485; *J.S.C.I.*, 1922, **41**, 573A; *Chem. Abs.*, 1922, **16**, 2630. S. D. Turner and J. W. Harrell, *Chem. Met. Eng.*, 1930, **37**, 98; *Chem. Abs.*, 1930, **24**, 2280; *Brit. Chem. Abs.* **B**, 1930, 357. W. Goldstern, *Petroleum Z.*, 1936, **32** (36), 1; *Brit. Chem. Abs.* **B**, 1936, 1028.

[224] K. M. Watson and E. F. Nelson, *loc. cit.*

[225] V. Kistyakovskii, *Z. physik. Chem.*, 1923, 107, 65; *Chem. Abs.*, 1924, **18**, 932; *J.C.S.*, 1924, **126** (2), 19.



Courtesy Universal Oil Products Co.

FIG. 341.—Chart for Specific Heats of Liquid Petroleum Fractions. (G. Egloff and E. F. Nelson)

tion, Watson and Nelson have plotted Fig. 342, in terms of the molal average boiling point and the characterization factor or the molecular weight. However, these investigators advocate, whenever possible, the use of the actually determined molecular weights in preference to the characterization factors curves (the latter involve the estimation of the molecular weight from Fig. 328). They state that the data obtained from Fig. 342 are in good agreement with the experimentally obtained values for the latent heat of vaporization obtained by Weir and Eaton[226] on both Mid-Continent and cracked stocks.[227]

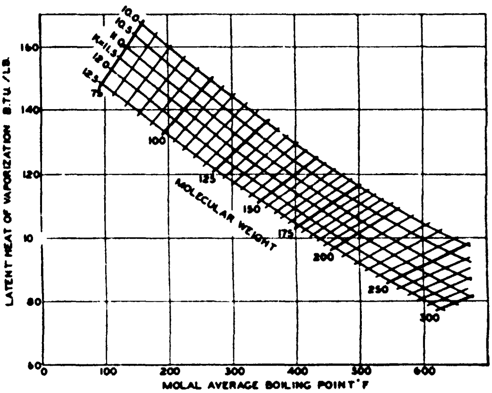


FIG. 342.
Diagram for Latent Heats of Vaporization of Petroleum Fractions at Atmospheric Pressure. (K. M. Watson and E. F. Nelson)

Courtesy Industrial and Engineering Chemistry

HEAT CONTENT

From their experiments on straight run gas oil stocks, Weir and Eaton[228] proposed the equation:

$$H = (215 - 87s) + (0.415 - 0.104s)t + (0.000310 - 0.000078s)t^2$$

where H = total heat above 32°F. (B.t.u. per lb.), s = specific gravity at 60°F. and t = temperature (°F.), for evaluating the total heats of gas oil vapors above 32°F. Gary, Rubin and Ward[229] have arrived at a similar relation for the total heat of liquid gas oil stocks:

$$H = (15s - 27) + (0.7615 - 0.400s)t + (0.000625 - 0.000440s)t^2$$

The latter authorities have plotted these two functions, as shown in Fig. 343, in terms of the A.P.I. gravity of the fractions. Thus, from this chart it is possible to estimate the input heat required to raise an oil of this nature to a given temperature knowing only the gravity. Gary, Rubin and Ward emphasize the fact that this figure should not be used for cracked stocks, as it is impossible to correlate the heat content data of different types of stocks by means of the specific gravity and temperature relations alone.

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[226] H. M. Weir and G. L. Eaton, *loc. cit.*

[227] W. C. Edmister (*Oil and Gas J.*, 1932, **30** (41), 50, 99; *Chem. Abs.*, 1932, **26**, 3366) has prepared a chart showing the latent heats and vapor pressures of a large number of pure hydrocarbons.

[228] H. M. Weir and G. L. Eaton, *loc. cit.*

[229] W. W. Gary, L. C. Rubin and J. T. Ward, *Ind. Eng. Chem.*, 1933, **25**, 178; *Brit. Chem. Abs.* **B**, 1933, 293; *Chem. Abs.*, 1933, **27**, 1492. See also A. J. E. Swann, *Fuel*, 1932, 11, 113; *Chem. Abs.*, 1932, **26**, 3654; *Brit. Chem. Abs.* **B**, 1932, 409.

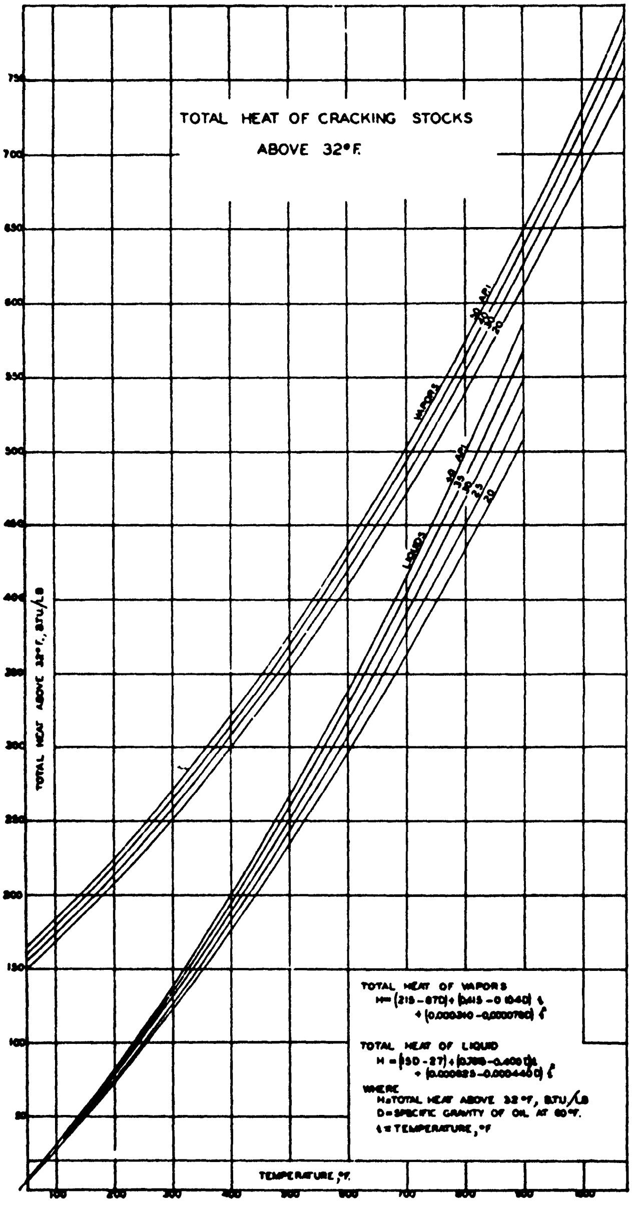

Fig. 343. Total Heat Chart for Gas-Oil Cracking Stocks. (W. W. Gary, L. C. Rubin and J. T. Ward)

Courtesy Industrial and Engineering Chemistry

Effect of Pressure on Heat Content of Hydrocarbon Vapors. A simple means for correcting the heat contents of gases and vapors for the effect of pressure has been proposed by Watson and Nelson.[230] By a combination of the basic thermodynamic equation

$$\left[\frac{\delta H}{\delta P}\right]_T = V - T\left[\frac{\delta V}{\delta T}\right]_P$$

expressing the rate of change of heat content with respect to pressure at constant temperature, and the corrected equation of state

$$PV = \mu RT$$

these workers obtained a relation of the type

$$\frac{\Delta HM}{T} = f(T_r,P_r)$$

where ΔH = change in heat content due to a change in pressure, M = the molecular weight of the fraction, T = absolute temperature (°R.) and $f(T_r,P_r)$ is a function of the reduced temperature and pressure only. Fig. 344, in which the ratio $\frac{\Delta HM}{T}$ is plotted against the reduced pressure and temperature, represents this relationship as introduced by Watson and Nelson. These curves have subsequently been revised by Egloff and Nelson,[231] as shown in Fig. 345. Thus, for a given reduced temperature and pressure, a value of the above ratio is read from the chart. This expression may now be solved for ΔH and the latter quantity subtracted from the heat content at atmospheric pressure to give the corresponding heat content for the vapor at the assumed pressure.[232]

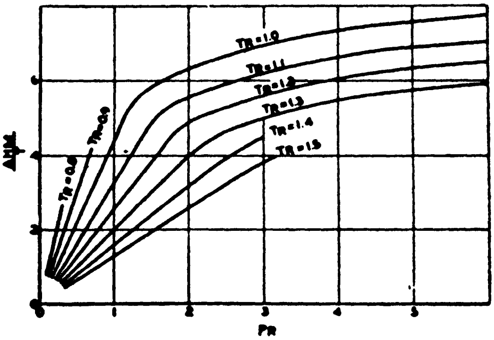

FIG. 344.
Heat Content Correction for Change in Pressure of Hydrocarbon Vapors. (K. M. Watson and E. F. Nelson)

Courtesy Industrial and Engineering Chemistry

Examples of Estimation of Total Heat Content. From the data and charts given on the preceding pages it is possible to obtain the total heat content of either liquid or vapor petroleum fractions over quite a broad range of temperature and pressure. It now remains to illustrate the general principles involved in the use of such information. Egloff and Nelson[233] have suggested several general procedures for problems of this type. For instance, the heat content

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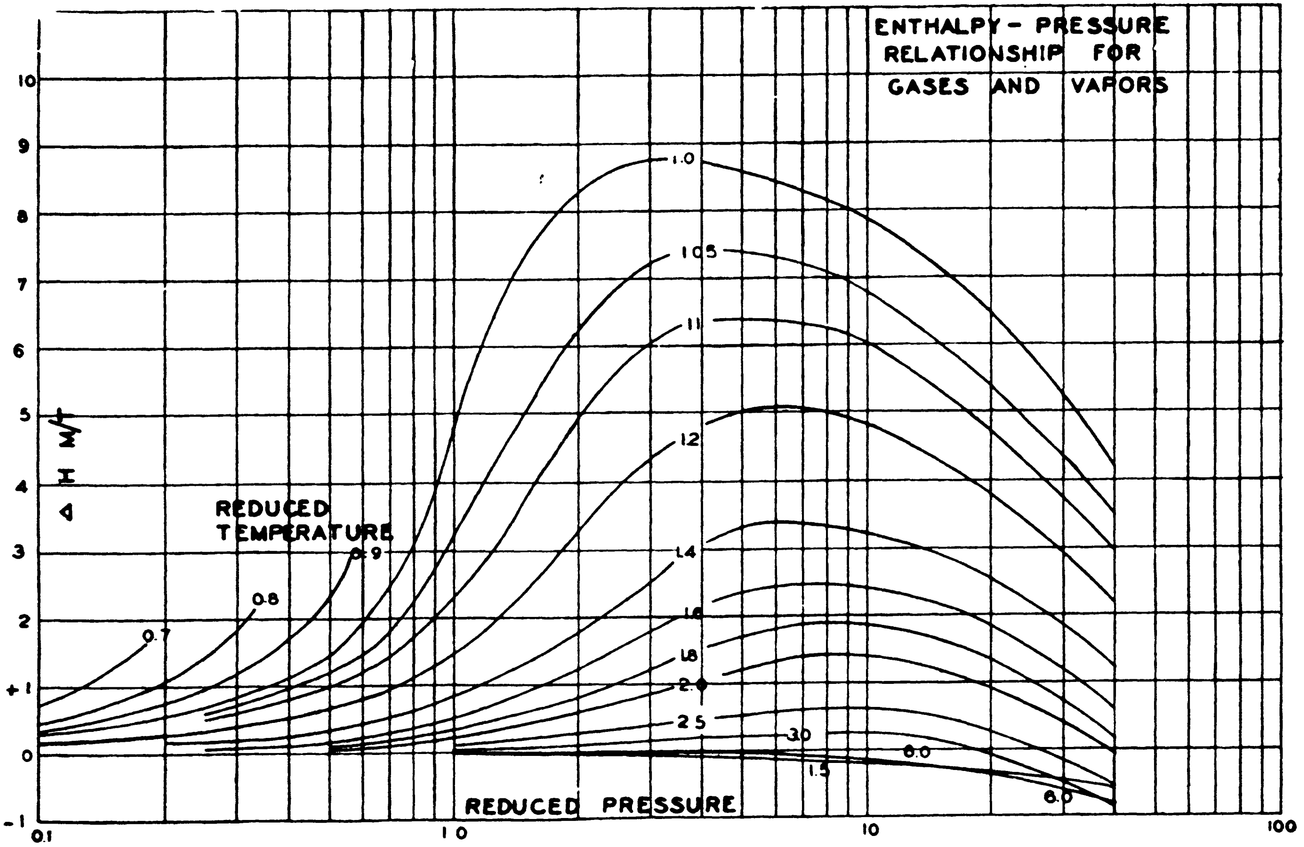
[230] K. M. Watson and E. F. Nelson, *loc. cit.*

[231] G. Egloff and E. F. Nelson, *Oil and Gas J.*, 1936, 35 (7), 34; *Chem. Abs.*, 1936, 30, 7828. Also "The Modern Cracking Process," Universal Oil Products Co., Chicago, 1936.

[232] According to Watson and Nelson, for ordinary calculations, the difference between heat content at zero and atmospheric pressures may be disregarded.

[233] G. Egloff and E. F. Nelson, *loc. cit.*



Courtesy Universal Oil Products Co.

FIG. 345.—Revised Chart of Heat Content Corrections for Pressure Change of Hydrocarbon Vapors. (G. Egloff and E. F. Nelson)

may be calculated at atmospheric pressure and the desired temperature and then corrected for the effect of pressure by means of Fig. 345. Or it may be assumed that the fraction is heated as a liquid to its average boiling point, vaporized at that temperature, and superheated as a vapor to the final temperature. (According to these collaborators, the errors introduced by this assumption are ordinarily negligible.) In the case of mixed-phase systems, however, the enthalpies of the liquid and vaporized portions are best treated separately.

As an illustration of the general use of the various charts, that cited by Watson and Nelson[234] using the data of Weir and Eaton[235] obtained for a naphtha fraction (volumetric average boiling point 256°F.) will be considered. The boiling characteristics of this stock, together with the calculated critical temperature and pressure, have already been given[236] and may be summarized as:

Specific gravity	0.7459
A.P.I. gravity	58
Molal average boiling point, °F.	241
Critical temperature, °F.	571
Critical pressure, lbs./sq.in. (absolute)	530

The characterization factor is calculated[237] as

$$K = \frac{(241 + 460)^{1/3}}{0.7459} = 11.9$$

This stock is therefore a typical Mid-Continent fraction, and so either Fig. 340 or 341 may be used directly to obtain the specific heats. From Figs. 328, 329 or 332 the molecular weight may be estimated as 108.

Assuming that it is desired to calculate the heat content above 32°F. for this naphtha in the vapor state at 800°F. and 1000 lbs. per sq. in. (gage pressure), from Fig. 341 the mean specific heat for the liquid between 32 and 241°F. (average boiling point) is obtained at the mean temperature, 137°F., as 0.532. The mean specific heat of the vapor between 241 and 800°F. is estimated from Fig. 340 at the mean temperature (520°F.) as 0.600. The heat of vaporization at 241°F. and $K = 11.8$ may be read from Fig. 342 as 133 B.t.u. per lb. The total heat content at atmospheric pressure, therefore, is given by:[238]

	B.t.u./lb.
Heat of liquid: $0.532(241 - 32) =$	111
Heat of vaporization	133
Heat of vapor: $0.600(800 - 241) =$	335
	579

To evaluate the total heat content at a gage pressure of 1000 lbs. per sq. in., Fig. 344 is used with the following supplemental data:

$$T = 800 + 460 = 1260°\text{F.}$$
$$T_r = 571 + 460 = 1031°\text{R.}$$
$$P_0 = 1000 + 15 = 1015 \text{ lbs. per sq. in. (absolute)}$$

The reduced temperature is, therefore,

$$T_r = 1260/1031 = 1.22$$

and the reduced pressure,

$$P_r = 1015/530 = 1.92$$

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[234] K. M. Watson and E. F. Nelson, *Ind. Eng. Chem.*, 1933, **25**, 880; *Chem. Abs.*, 1933, **27**, 5522; *Brit. Chem. Abs.* **B**, 1933, 995; *J. Inst. Pet. Tech.*, 1933, **19**, 408A.

[235] H. M. Weir and G. L. Eaton, *Ind. Eng. Chem.*, 1932, **24**, 211; *Brit. Chem. Abs.* **B**, 1932, 327; *Chem. Abs.*, 1932, **26**, 1760.

[236] See the section on Estimation of Critical Pressure.

[237] This value may also be obtained by interpolation from Fig. 332.

[238] From experimental data of H. M. Weir and G. L. Eaton, a value of 580 B.t.u. per lb. is given for this stock.

From these values of reduced pressure and temperature the ratio $\frac{\Delta HM}{T}$ is interpolated[289] from Fig. 344 as 4.65, and, therefore,

$$\Delta H = \frac{4.65 \times 1260}{108} = 54 \text{ B.t.u. per lb.}$$

The total heat content at 800°F. and 1000 lbs. per sq. in. is

$$579 - 54 = 525 \text{ B.t.u. per lb.}$$

THERMAL DIAGRAMS FOR HYDROCARBONS

The thermodynamic properties of a substance may be represented graphically in several different manners. Among the most common types of charts in general use that will be considered are enthalpy, temperature-entropy and Mollier diagrams. Each of these series of curves has advantages and special adaptability for different kinds of problems.

ENTHALPY DIAGRAMS

The enthalpy-pressure-temperature relations of hydrocarbons may be very conveniently tabulated in charts of the type of Figs. 346, 347, 348 and 349. In all of these diagrams, the pressure is plotted as ordinate and the temperature as abscissa. Lines of constant enthalpy (heat content or total heat) are represented by straight lines (nearly perpendicular to the temperature axis). In most thermal problems it is not necessary to know the absolute heat content, since only changes

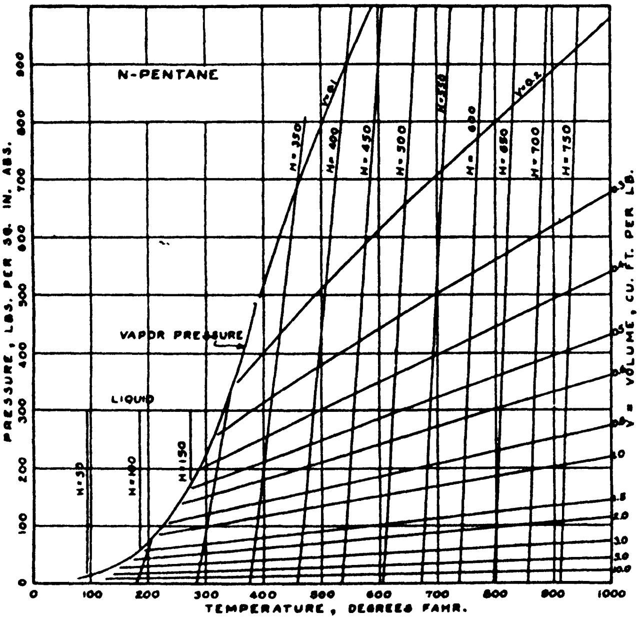

FIG. 346. Enthalpy Diagram for *n*-Pentane. (E. C. Pattee and G. G. Brown)

Courtesy Industrial and Engineering Chemistry

in the relative value are of importance. Therefore, it is arbitrarily assumed in these charts that at one definite set of conditions the heat content may be taken as zero. Ordinarily the datum conditions employed are a standard state (solid, liquid or gas, as the case may be) at 32° F.[240]

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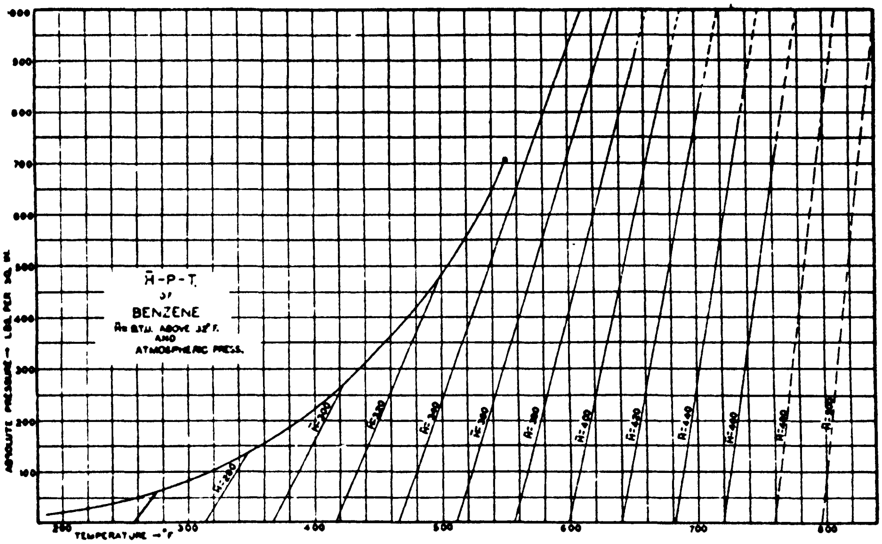
[289] Fig. 345, based on subsequent data, would give a lower value for this ratio.

The enthalpy diagram for *n*-pentane (see Fig. 346) was determined by Pattee and Brown[241] from experimental data. It is interesting to note the information presented by this chart. The pressure-temperature relation gives the vapor pressure curve. All points to the left of this line refer, therefore, to the liquid phase and those on the right to the vapor phase. In addition to the heat content lines, isochores (constant volume lines) are also included. Thus, from the temperature and pressure of *n*-pentane, it is possible to predict not only the state, but the heat content and volume occupied by the material.



Courtesy Industrial and Engineering Chemistry

FIG. 347.—Enthalpy-Pressure-Temperature Relationships of Benzene. (J. D. Lindsay and G. G. Brown)

The diagram shown in Fig. 347 was obtained by Lindsay and Brown[242] for benzene. (This chart differs from that of *n*-pentane in that the constant volume lines have been omitted.) Fig. 348 represents the data accumulated by Pattee and Brown[243] for a naphtha fraction[244] and is similar to Fig. 346 in its construction and applicability.

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[240] Thus, in the case of water, this is standard procedure ordinarily followed, i.e., water at 32° F. and normal pressure is arbitrarily assumed to have a heat content of 0. Following this convention, for conditions below datum, the heat content is regarded as a negative quantity. In petroleum technology, it is often more advantageous to set the datum temperature as 60° F. rather than 32° F. as in the case of water.

[241] E. C. Pattee and G. G. Brown, *Ind. Eng. Chem.*, 1934, **26**, 511; *J. Inst. Pet Tech.*, 1934, **20**, 400A; *Brit. Chem. Abs.* **B**, 1934, 567; *Chem. Abs.*, 1934, **28**, 4876.

[242] J. D. Lindsay and G. G. Brown, *Ind. Eng. Chem.*, 1935, **27**, 817; *Brit. Chem. Abs.* **B**, 1935, 791; *Chem. Abs.*, 1935, **29**, 7170; *J. Inst. Pet. Tech.*, 1935, **21**, 335A.

[243] E. C. Pattee and G. G. Brown, *loc. cit.*

[244] The type of naphtha used by these investigators was a so-called varnish maker's and painter's naphtha and had an A.S.T.M. distillation 50 per cent point of about 255°F. Using the method proposed by K. M. Watson and E. F. Nelson (see section on molecular weight) the equivalent hydrocarbon was found to be octane.

From the plots for *n*-pentane and naphtha, Pattee and Brown concluded that for practical purposes, a mixture of hydrocarbons may be treated approximately as a pure compound of the same critical temperature, pressure and molecular weight, as suggested by Watson and Nelson.[245] The former investigators also point out that although the results obtained by these approximations are by no means accurate, the correction due to pressure is so small in comparison with the effect of temperature on the enthalpy that the final result obtained is in all probability sufficiently accurate for most engineering purposes.

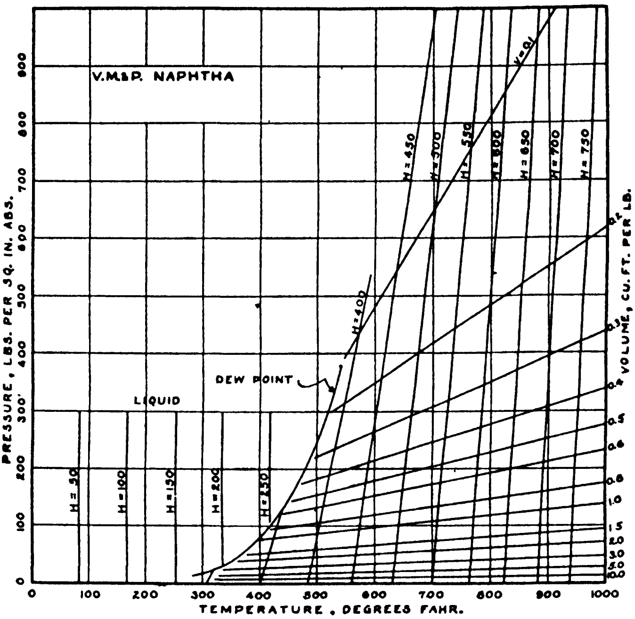


FIG. 348. Enthalpy Diagram for Naphtha Fraction. (E. C. Pattee and G. G. Brown)

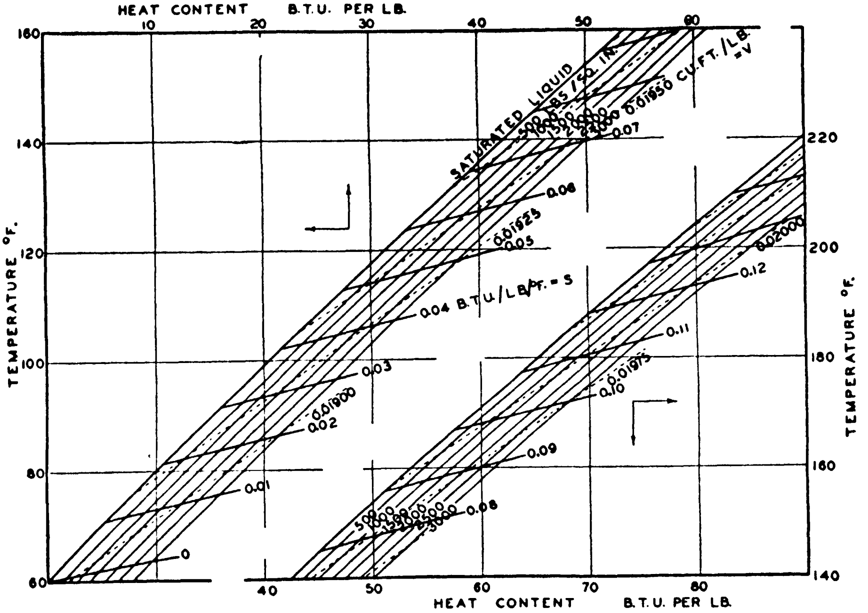
Courtesy Industrial and Engineering Chemistry

In Fig. 349 is shown a different type of enthalpy chart, one in which the heat content is plotted against the temperature for parametric values of the pressure. This particular series of curves were determined by Sage, Lacey and Schaafsma[246] for a California crude oil of specific gravity 0.8383 (37.1°A.P.I.) at 60°F. and a molecular weight of 188. In addition to the constant volume lines (indicated by dashes), constant entropy curves are also included on this chart. The double scale has been employed in order to enlarge the isothermal sections. It will be noted that the datum conditions for this graph are saturated liquid at 60°F. and 1 atmosphere. Sage, Lacey and Schaafsma have stated that the entropy-temperature plane is usually preferable for the graphical representation of the thermal properties of a substance. However, in this case, the isothermal changes in entropy are so small compared to the isobaric changes with temperature that the former properties cannot be properly shown in a temperature-entropy scale.

[245] K. M. Watson and E. F. Nelson, *Ind. Eng. Chem.*, 1933, **25**, 880; *Chem. Abs.*, 1933, **27**, 5522; *Brit. Chem. Abs.* **B**, 1933, 995; *J. Inst. Pet. Tech.*, 1933, **19**, 408A.

[246] B. H. Sage, W. N. Lacey and J. G. Schaafsma, *Ind. Eng. Chem.*, 1935, **27**, 162; *J. Inst. Pet. Tech.*, 1935, **21**, 122A; *Brit. Chem. Abs.* **B**, 1935, 886; *Chem. Abs.*, 1935, **29**, 2044.

Sage, Lacey and Schaafsma[247] have shown the applicability of Fig. 349 in estimating the change in heat content of an oil under conditions of adiabatic[248] and isothermal compression. Thus, the frictionless adiabatic compression of the oil follows along a line of constant entropy from the initial to the final state. On the other hand, the isothermal compression is represented by a horizontal path from the initial to the final pressure. In the first instance, the work done by the adiabatic compression is given by the gain in heat content of the fluid or by the graphical evaluation of $\int VdP$ over the constant entropy path. For the isothermal case, however, the gain in heat content is given by Fig. 349, and when the step is frictionless, the heat rejected is determined by ascertaining $T(S_1 - S_2)$ (where the subscripts refer to the initial and final stages, respectively) for the path. The sum of the heat gained and that rejected gives the work done.[249]



Courtesy Industrial and Engineering Chemistry

FIG. 349.—Temperature-Enthalpy Chart for a Crude Oil. (B. H. Sage, W. N. Lacey and J. G. Schaafsma)

TEMPERATURE-ENTROPY DIAGRAMS

Figs. 350, 351 and 352 are typical temperature-entropy diagrams for hydrocarbons.[250] These curves are usually plotted with temperature as ordinate and

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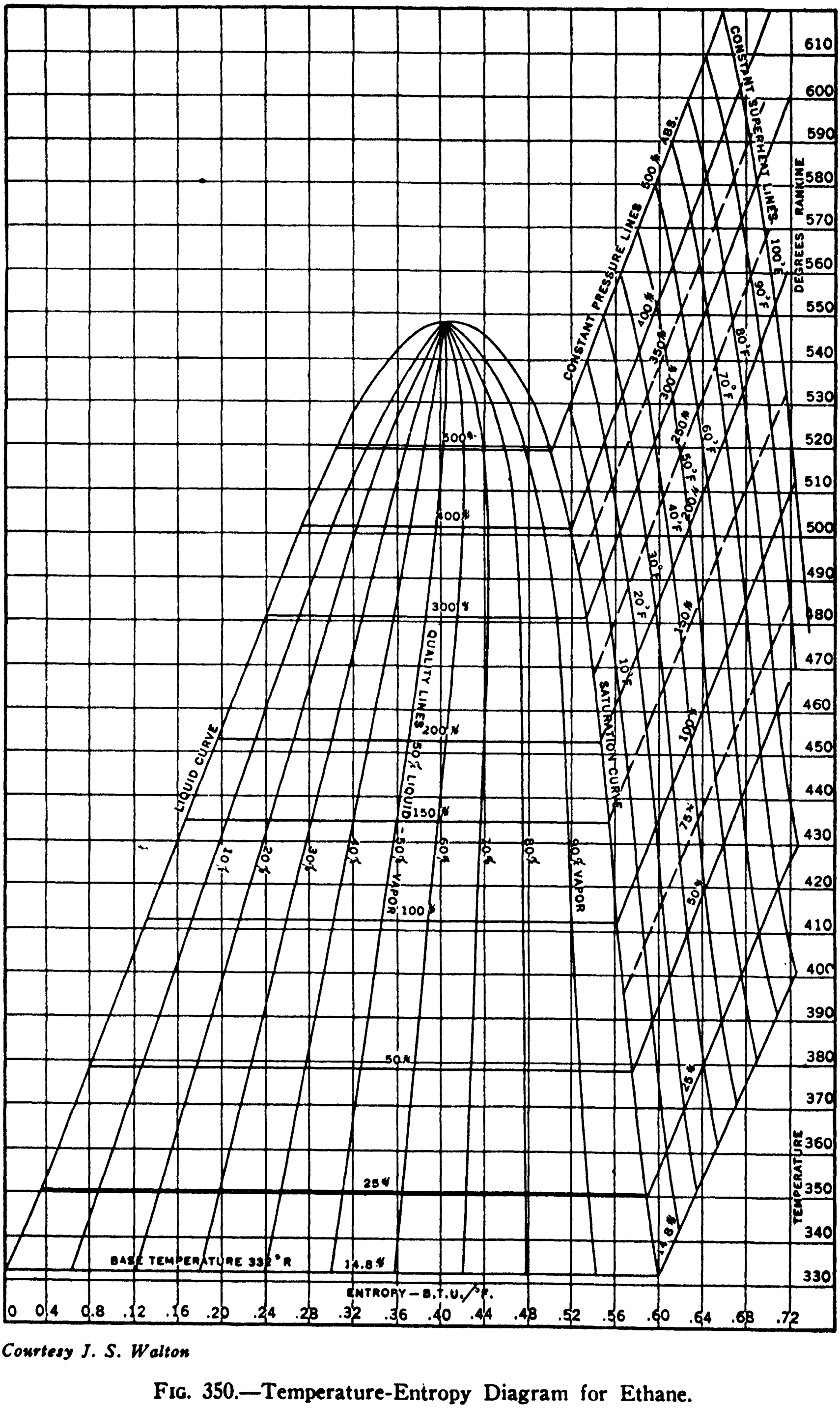
[247] B. H. Sage, W. N. Lacey and J. G. Schaafsma, *loc. cit.*

[248] An adiabatic transformation is defined as one in which there is no exchange of heat with respect to the surroundings, that is, heat neither enters nor leaves the system during transformation.

[249] For other general examples see: W. H. Walker, W. K. Lewis and W. H. McAdams, "Principles of Chemical Engineering," McGraw-Hill Book Co., Inc., New York and London, 1923. J. H. Perry, "Chemical Engineers' Handbook," McGraw-Hill Book Co., Inc., New York and London, 1934.

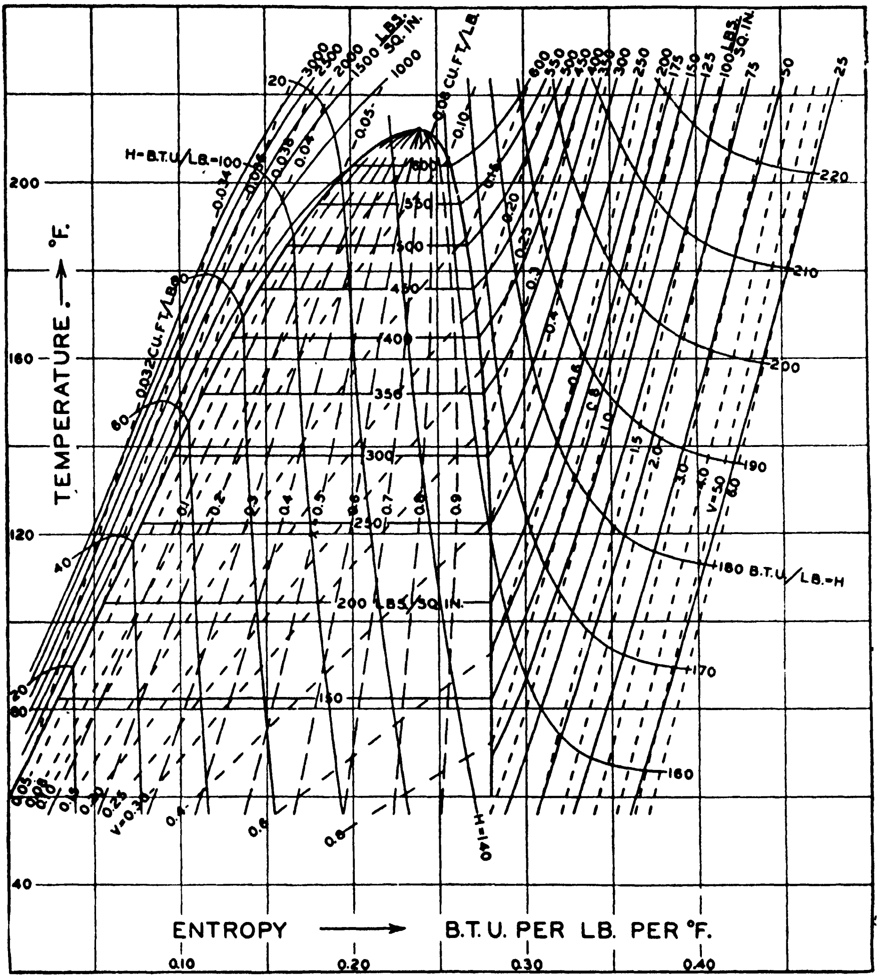
[250] Temperature-entropy diagrams for water, ammonia, carbon dioxide, air, hydrogen, helium, nitrogen, methane and ethylene will be found in J. H. Perry, "Chemical Engineers' Handbook," McGraw-



Courtesy J. S. Walton

FIG. 350.—Temperature-Entropy Diagram for Ethane.

entropy as abscissa. Lines of constant pressure, constant volume and constant enthalpy are usually also included on these charts. According to Lacey and Sage,[251]



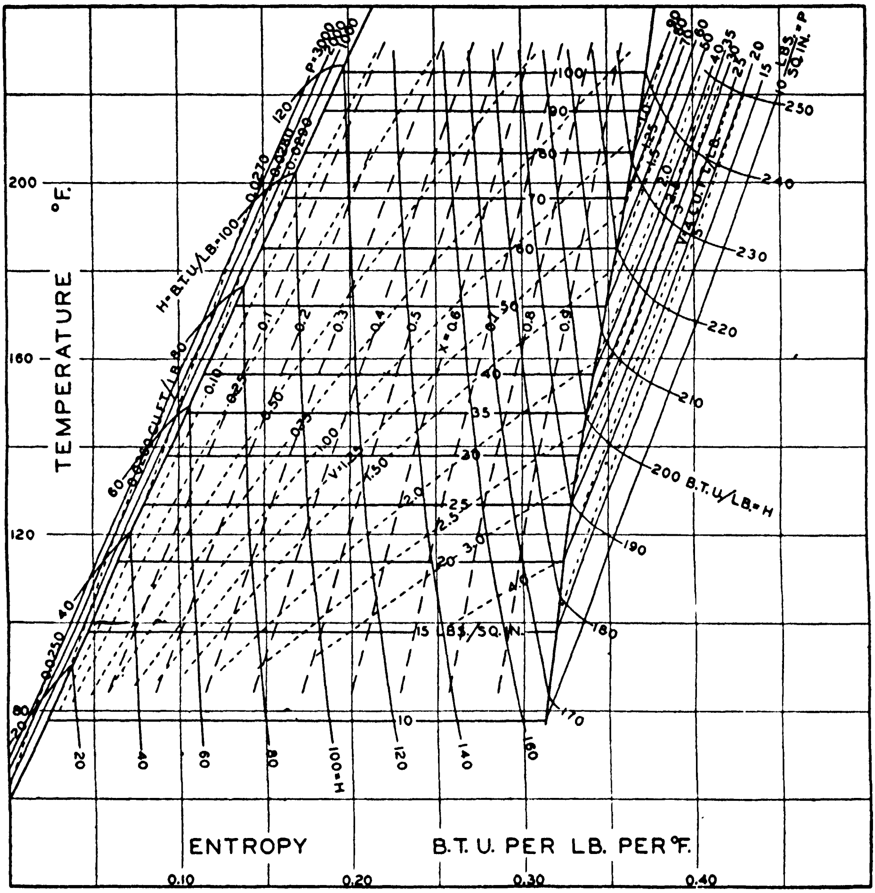
Courtesy Industrial and Engineering Chemistry

FIG. 351.—Temperature-Entropy Diagram for Propane. (B. H. Sage, J. G. Schaafsma and W. N. Lacey)

Hill Book Co., Inc., New York and London, 1934. S. Sugawara and R. Nozawa, (*Trans. Soc. Mech. Engrs.* (*Japan*), 1936, 2, 359; *Chem. Abs.*, 1936, 30, 7022) prepared an entropy chart for dichloromethane. W. C. Edmister (*Ind. Eng. Chem.*, 1936, 28, 1112; *Brit. Chem. Abs.* A, 1936, 1330; *Chem. Abs.*, 1936, 30, 7437; *J. Inst. Pet. Tech.*, 1936, 22, 538A.) calculated a table of entropy and enthalpy values for methane. I. N. Beall (*Refiner*, 1935, 14, 77; *Chem. Abs.*, 1935, 29, 2714) tabulated data for the lower hydrocarbons, and also for isobutane (*Refiner*, 1935, 14, 437; *Chem. Abs.*, 1935, 29, 7779). Detailed instructions for the construction of temperature-entropy diagrams and an example (using methane) have been given by J. H. C. Lisman (*Koeltech.*, 1935, 6, 1; *Chem. Abs.*, 1936, 30, 7437).

[251] W. N. Lacey and B. H. Sage, *Oil and Gas J.*, 1934, 33 (26), 86; *Chem. Abs.*, 1935, 29, 585; *J. Inst. Pet. Tech.*, 1935, 21, 10A.

slightly to the center of Fig. 351 (for propane) will be seen the so-called "saturation dome," with the critical point at its apex (the critical temperature for propane is approximately 212°F.). The left-hand side of this line corresponds to the case of liquid propane at its vapor pressure (saturation line.) The right-hand side refers to saturated propane gas. The region beneath the dome applies to equilibrium mixtures containing both liquid and gas phases. The portion of the diagram to the left of the dome describes the behavior of liquid propane at pressures greater



Courtesy *Industrial and Engineering Chemistry*

FIG. 352.—Temperature-Entropy Diagram for *n*-Pentane. (B. H. Sage, W. N. Lacey and J. G. Schaafsma)

than its vapor pressure, and that on the right of the dome relates to information concerning superheated propane gas.

The nearly vertical solid lines (labeled near the top of the figure) are isobars, or lines of constant pressure. Within the saturation dome these lines become nearly horizontal. This is due to the fact that a pure substance undergoes a transition of state (such as from liquid to vapor, or vice versa) at constant temperature and pressure. The short-dash lines indicate values of constant specific volume (cu.ft. per lb. in this case) or isochores. When both liquid and gas phases are present (that is, within the dome), these lines indicate the specific volume of the whole mixture. The long-dash lines (within the dome) meeting at the critical point are lines of constant quality[252] (constant mass fraction of the mixture which is in the gaseous state under the conditions prevailing). The solid lines which slope downward to the right are lines of constant heat content (enthalpy or total heat). Neither the entropies nor enthalpies indicated on this chart are absolute values. Both quantities are based on an arbitrary datum of saturated liquid propane at 60° F.

Fig. 350 represents the temperature-entropy diagram for ethane, as obtained by Walton.[253] The curves for propane, Fig. 351, described previously are the results of investigations conducted by Sage, Schaafsma and Lacey.[254] Fig. 352 for pentane was constructed by Sage, Lacey and Schaafsma[255] from experimental data. (In this instance, the saturation dome has not been included in the figure.)

As an example of the use of these diagrams, the illustration of Lacey and Sage,[256] involving the application of Fig. 351, will be considered. Assume that a sample of propane is at a temperature of 180° F. and occupies a volume per pound of 0.10 cu. ft. By locating the position on the diagram where these two conditions are fulfilled, it will be found that propane exists in the proportions of 0.56 lb. of liquid and 0.44 lb. of gas per lb. of mixture. The pressure is approximately 470 lbs. per sq. in. (absolute), the heat content is 123 B.t.u. per lb. and the entropy is 0.204 B.t.u. per lb. per degree Rankine (Fahrenheit, absolute). This diagram is also useful in problems involving continuous processes, as indicated by Lacey and Sage in the following example. Assume that the above sample of propane passes through a continuous flow system, such that the final conditions find the sample at 80° F. and an absolute pressure of 50 lbs. per sq. in. From the chart it will be found that this hydrocarbon will exist entirely as a gas with a specific volume of 2.55 cu. ft. per lb., a heat content of 164 B.t.u. per lb. and an entropy of 0.347 B.t.u. per lb. per degree Rankine.

To illustrate the further use of this chart, these collaborators assume (arbitrarily) that the last mentioned system consists of the flow of propane through a continuous vertical pipe, 4000 ft. long, and that both the decrease in pressure and the heat gained or lost through the wall are directly proportional to the distance travelled in the pipe. In this case, the useful work of lifting amounts to 4000 ft. lbs. per lb. of propane, which is equivalent to 5.1 B.t.u. per lb. In such a flowing system, the difference between the final and initial heat contents gives the net increase or net decrease in energy in the moving fluid. In the assumed case, the increment is $164 - 123 = 41$ B.t.u. per lb. This net increase in energy, despite the fact that useful work has been done, indicates that energy (in the form of heat) has been added to the fluid through the walls of the pipe. The amount of heat absorbed must then be $41 + 5.1 = 46.1$ B.t.u. per lb.

On the basis of the supposed conditions relating to the change of pressure and heat gained through the walls, it is possible to follow the path of the change occurring during the step. As a result of this, the corresponding values of temperature and entropy may be read from the chart for any stage in the operation. By reading a series of such values and plotting them with entropy as abscissa and the absolute temperature as ordinate, the area below the resulting curve between the initial and final states may be determined, and in this manner the value of the sum of heat absorbed through the walls and the heat developed as the result of friction may be obtained. (The friction results both from turbulence within the fluid and from movement of the mixture relative to the interior pipe wall.) For the above case, Lacey and Sage found this sum to be 81.4 B.t.u. per lb. Since the heat absorbed was 46.1 B.t.u. per lb., the heat developed as a result of friction is

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[252] Thus, in the case of steam tables, the "quality" is indicative of the percentage of steam actually present under the conditions.

[253] J. S. Walton, *Refiner,* 1935, **14**, 440; *Chem. Abs.,* 1935, **29**, 7779.

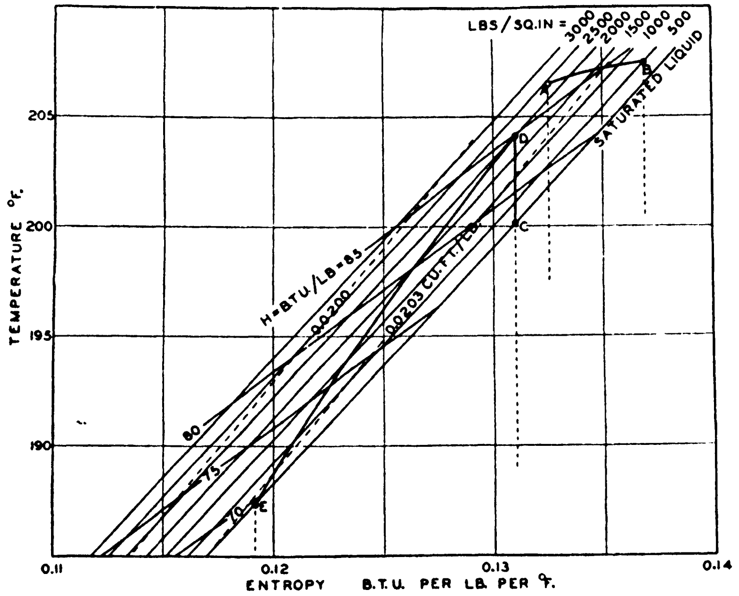
[254] B. H. Sage, J. G. Schaafsma and W. N. Lacey, *Ind. Eng. Chem.,* 1934, **26**, 1218; *J. Inst. Pet. Tech.,* 1934, **20**, 606A; *Brit. Chem. Abs.* **A**, 1935, 22; *Chem. Abs.,* 1935, **29**, 28. A temperature-entropy chart for propane has also been constructed by E. Justi (*Z. Ver. deut. Ing.,* 1936, **80**, 103; *Chem. Abs.,* 1936, **30**, 7097).

[255] B. H. Sage, W. N. Lacey and J. G. Schaafsma, *Ind. Eng. Chem.,* 1935, **27**, 48; *Chem. Abs.,* 1935, **29**, 670; *J. Inst. Pet. Tech.,* 1935, **21**, 90A; *Brit. Chem. Abs.* **A**, 1935, 290.

[256] W. N. Lacey and B. H. Sage, *Oil and Gas J.,* 1934, **33** (26), 86; *Chem. Abs.,* 1935, **29**, 585; *J. Inst. Pet. Tech.,* 1935, **21**, 10A.

$$81.4 - 46.1 = 35.3 \text{ B.t.u. per lb.}$$

This quantity of heat has been produced at the expense of energy otherwise available for doing useful work. Another way in which the energy is utilized is by increasing the velocity of the moving fluid. The energy required for this purpose is ordinarily quite small, and in the assumed instance would be approximately 0.2 B.t.u. per lb. if the final velocity is taken as 100 ft. per sec.[257]



Courtesy Industrial and Engineering Chemistry

FIG. 353.—Temperature-Entropy Chart for a Crude Oil. (B. H. Sage, W. N. Lacey and J. G. Schaafsma)

Fig. 353 is a temperature-entropy diagram for a California crude oil (37.1° A.P.I. gravity) as determined by Sage, Lacey and Schaafsma[258] from experimental data. These investigators also point out the value of charts of this nature.

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[257] For other examples, see J. H. Perry, "Chemical Engineers' Handbook," McGraw-Hill Book Co., Inc., New York and London, 1934. W. H. Walker, W. K. Lewis and W. H. McAdams, "Principles of Chemical Engineering," McGraw-Hill Book Co., Inc., New York and London, 1923.

[258] B. H. Sage, W. N. Lacey and J. G. Schaafsma, *Ind. Eng. Chem.*, 1935, 27, 162; *J. Inst. Pet. Tech.*, 1935, 21, 122A; *Brit. Chem. Abs.* B, 1935, 886; *Chem. Abs.*, 1935, 29, 2044.

Thus, the random path *AB* could represent any one of a number of operations. If there is no work done on or by the system, or no change in elevation, the difference in the initial and final heat contents will give the loss of heat from the oil in going from *A* to *B*. The graphically determined value for $\int TdS$ added to the loss in heat content gives the amount of heat produced as the result of friction in the step represented by the path between *A* and *B*. (If the change in elevation or the work done by the oil is known, it can be added to or subtracted from the change in heat content, and the above method can be used to determine the friction.)

The principles outlined by these workers can be illustrated by a specific problem, such as that shown by the path *CDE*. This path may be assumed to be that of a pumping oil well, operating under arbitrarily chosen conditions. Let point *C* represent the condition of the oil at the entrance to the pump cylinder, 4000 ft. below the surface, assuming it to be a liquid at 200.1°F. under the saturation pressure. Point *D* represents the conditions at the outlet of the pump cylinder (corresponding to a pressure of 2000 lbs. per sq. in. after a frictionless adiabatic step, that is, the entropy of the oil at the entrance and outlet of the pump cylinder is the same). The work done in this step is equal to the difference in the initial and final heat content, or 7.5 B.t.u. per lb. of oil. (As a check, the work may be calculated by evaluating $\int VdP$, and is found to be 7.37 B.t.u.) Let point *E* represent the state of the oil at the surface, with a temperature of 187.4°F. and under the corresponding saturation temperature. The path *DE* is arbitrarily chosen to represent the thermodynamic path of the fluid up the pipe line.[259] The difference in enthalpy between *D* and *E* (14.80 B.t.u.) measures the heat lost to the surroundings (in this case, 9.66 B.t.u. per lb. of oil.) The value of $\int TdS$ over the given path from *D* to *E* is found (by graphical integration) to be —7.78 B.t.u. per lb. Then the energy lost as a result of friction during flow is equal to the algebraic sum of $\int TdS$ and the heat lost by the system, and in this instance is equal to 1.88 B.t.u. per lb. of oil.

MOLLIER DIAGRAMS

Mollier diagrams are plotted between heat content as ordinate and entropy as abscissa, and are especially adapted to problems involving flow of fluids. As Walton[260] has pointed out, although on entropy-temperature charts heat quantities are represented by areas, on diagrams of the Mollier type they are shown by line segments. It is also customary to include lines of constant quality, constant superheat, isobars, isotherms and isochores on these depictions.

Fig. 354 represents the Mollier diagram for ethane, as obtained by Walton.[261] The datum temperature for this chart is 332°R. (—128°F.). As an example of the application of the data included in this figure, Walton has considered the following problem. It is desired to determine the condition of the vapor resulting in the expansion (through a valve) of a mixture composed of 95 per cent ethane vapor and 5 per cent ethane liquid at 85.3 lbs. per sq. in. gage pressure to atmospheric pressure (14.8 lbs. per sq. in. absolute). This is an expansion of the Joule-Thomson type, occurring at constant total heat. Thus, from the intersection of the 100 lbs. per sq. in. absolute pressure line and the 95 per cent quality line, the constant heat curve is followed across the diagram to the right until the 14.8 lbs.

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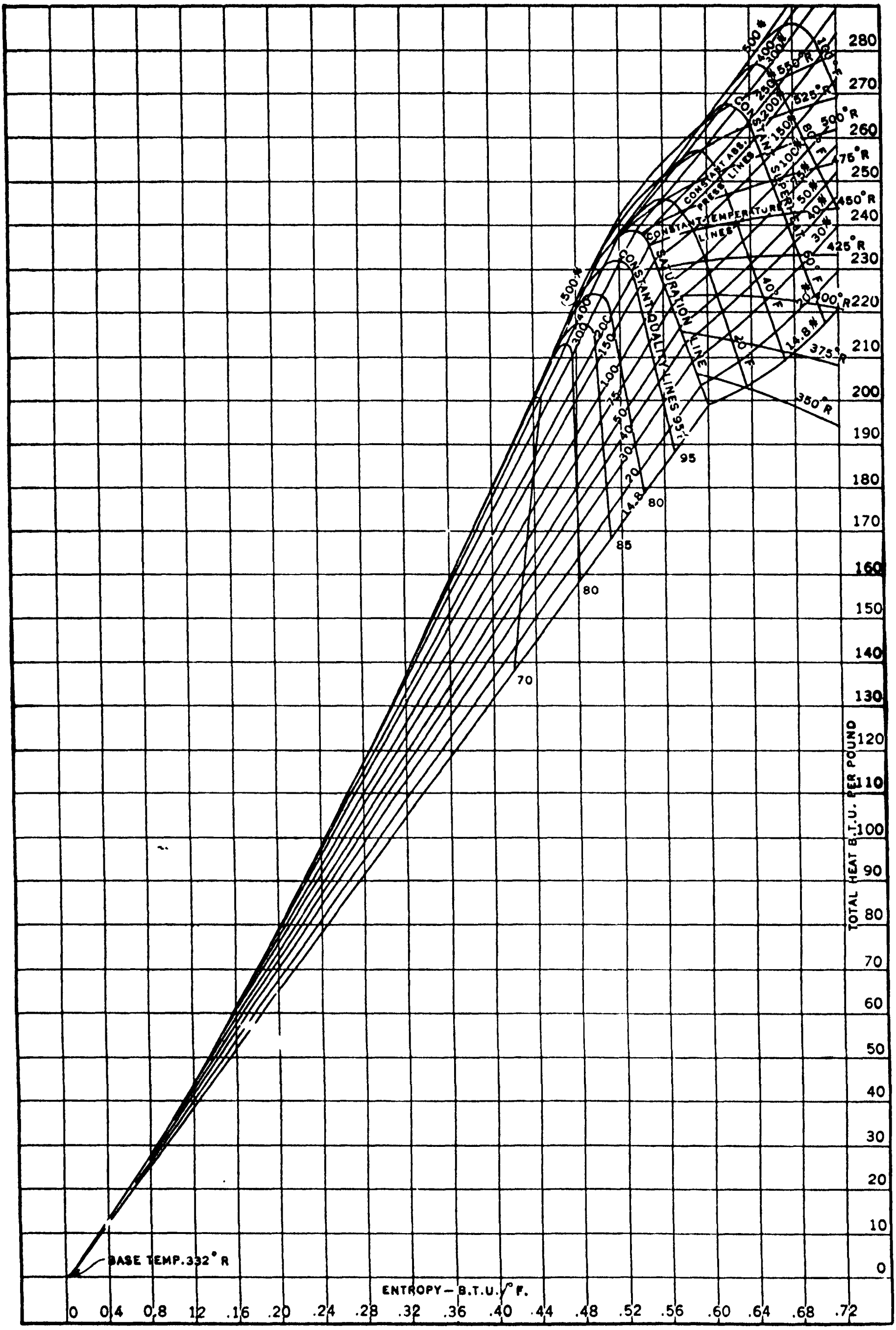
[259] The thermodynamic properties are dependent only on the initial and final state, and not on the path. However, the exact path is necessary for the evaluation of the friction.

[260] J. S. Walton, *Refiner*, 1935, 14, 440; *Chem. Abs.*, 1935, **29**, 7779. This article should be consulted for an explanation of the manner of derivation of both Mollier and temperature-entropy diagrams from tables of thermodynamic data. Mollier diagrams for ammonia, carbon dioxide, air, ethylene, helium, hydrogen, methane, nitrogen and steam have been given by J. H. Perry, "Chemical Engineers' Handbook," McGraw-Hill Book Co., New York and London, 1934.

[261] J. S. Walton, *loc. cit.*



Courtesy J. S. Walton

FIG. 354.—Mollier Diagram for Ethane.

per sq. in. isobar is reached. At this point on the chart it will be seen by interpolation that ethane exists as a superheated vapor at —70° F. and has a superheat of 62° F.

As another example, Walton[262] has calculated the work done in the reversible expansion of 57 lbs. of ethane vapor at 200 lbs. per sq. in. absolute pressure and 475°R. (15°F.) to 30 lbs. per sq. in pressure in an engine, without appreciable loss or gain of heat. Since this is an adiabatic expansion, there will be no change in entropy. The initial heat content of the ethane is read from Fig. 354 as 242.5 B.t.u. per lb. Following down the constant entropy line to the 30 lbs. per sq. in. isobar, the final heat content is given as 206.5 B.t.u. per lb. The available work is, therefore,

$$242.5 - 206.5 = 36 \text{ B.t.u. per lb.}$$

or

$$(36 \times 57) = 2052 \text{ B.t.u.}$$

from the 57 lbs. of ethane. On multiplying this value by the conversion factor, 778, to give foot pounds, the amount of work available is given as

$$(778 \times 2052) = 1{,}596{,}000 \text{ ft. lbs.}$$

The quality of the final mixture may be read by interpolating between the constant quality lines as 98.5 per cent.

As indicated above, the application of thermodynamics to the petroleum field is limited to some extent since the element of reaction time does not enter into this type of calculation. Also, a number of the factors employed are probably subject to considerable error. Nevertheless, in many instances thermodynamic considerations frequently serve to foretell, to a reasonable extent, the probability of a given course of reaction. It is apparent that, as more accurate data come to hand, this phase of the petroleum industry will gradually develop to one of great significance.

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[262] J. S. Walton, *loc. cit.*

Name Index

A

Abakova, E. S., 1164
Abbott Laboratories, 540
Abelmann, L. E., 889
Abezgauz, I., 495
Abkin, A., 674, 727, 728, 796
Aborn, R. H., 1165
Aboulenc, J., 806
Abraham, A., 728, 745
Abraham, H., 46
Abramovich-Dvoretzkaya, R. M., 1114
Abrams, V. R., 469
Abugov, D., 1007
Aceta G. m. b. H., 588
Acker, A., 932, 935
Ackert, J. E., 733
Adadurov, I. E., 331
Adal'yan, L. K., 1055
Adam, L., 138, 179
Adams, C. E., 46, 816
Adams, R., 540, 764, 771, 1082
Adamyan, L. K., 476, 1116
Adico Development Corp., 539, 578
Adkins, H., 340, 346, 350, 351, 369, 372, 546, 621, 878
Adler, I., 852
Advani, G. D., 1111
Afanas'ev, B. N., 700
Afanasyev, I. D., 1173
Agulhon, H., 354
Aicher, A., 1230, 1234, 1237, 1238, 1239, 1248
Aichner, F., 550
Aikawa, H., 703
Air Reduction Co., 161, 163, 169, 282, 283, 291
Aivazov, B., 994
Aiyar, S. S., 371
Akashi, M., 245
Åkerlöf, G., 580
Akestorides, F., 622
Akita, Y., 849, 999
Akobzahanov, I. G., 673
Aktiebolaget Separator-Nobel, 434, 495, 710, 914
Aktiengesellschaft für medizinische Produkte, 747
Aktis A.-G., 131
Al'bitzkaya, O. P., 948
Albrecht, H. O., 576
Albright, J. C., 24, 26, 125, 668
Alco Products, Inc., 191
Alden, R. C., 27, 1017, 1169
Alder, K., 652, 688
Aldoshin, T. D., 779
Aldrich, E. N., 1315
Aldridge, B. G., 1201, 1204
Aldrin, E. E., 378, 380, 1039
Alekhina, A. P., 709
Aleksandrov, L. A., 108, 135, 912, 1156
Aleksandrovich, D., 458
Alekseev, S. V., 173, 347, 509, 510, 516, 627, 753
Alekseeva, E. N., 381
Alekseevskii, E. V., 337, 793
Alexander, D. B. W., 1193
Alexander, L. L., 207
Alexander & Posnansky, Firm., 468
Alfimova, E., 1104
Algard, G., 710, 790
Aliev, P. M., 1090
Allan, H. L., 1205
Alleman, G., 823, 1018, 1107
Allen, A. H., 1171
Allen, A. O., 426
Allen, A. S., 574
Allen, C. C., 451, 462, 472
Allen, R. G., 237
Allibone, B. C., 925
Allner, W., 573
Allott, E. N., 886
Almquist, J. A., 949
Alox Chemical Corp., 968, 969, 972, 1059, 1061
Alquier, R., 721
Alvarado, A. M., 496
Amarel Corp., 1056
Ambuhl, G., 1096
American Bitumuls Co., 1218
American Colloid Co., 790
American Cyanamid & Chemical Corp., 789, 915, 960
American Cyanamid Co., 279, 394, 889
American Enka Corp., 578, 1076
American Lurgi Corp., 636
American Rolling Mill Co., 1205
American Soap and Glycerine Producers, 544
American Tar Products Co., Inc., 434
Amiesite Asphalt Co. of America, 1216
Ammonia Casale S. A., 705
Amthor, F., 790
Amusin, M. K., 828
Anantakrishnan, S. V., 503, 508
Andant, A., 32, 33
Anderson, A. P., 38, 44, 1201
Anderson, C. C., 1126
Anderson, C. T., 1279
Anderson, D. Q., 19
Anderson, E., 889
Anderson, J. A., 348, 575, 758, 817
Anderson, J. S., 628
Anderson, W. P., 362
Anding, C. E., Jr., 1158
André, E., 40, 756, 759
Andreev, D. N., 72, 87, 202, 643
Andreev, E. A., 873, 1123, 1124, 1125, 1142
Andreev, I., 668
Andreev, N. Z., 347, 651
Andreeva, A. I., 975
Andreeva, E., 209
Andreevskii, D. N., 180
Andrevskii, I. L., 930
Andrews, C. W., 230
Andrussow, L., 281, 794, 871
Aneus, W. R., 441
Anfinogenov, P. Z., 146
Anglo-Iranian Oil Co., Ltd., 42, 215
Anglo-Persian Oil Co., Ltd., 478, 533, 550, 915, 917
Angstadt, H. F., 1107
Anisimov, S. B., 420
Annable, W. G., 489
Annaratone, D., 1039
Anschütz, R., 208, 885
Antares Trust Registered, 445, 446
Antheaume, J., 1231
Antzus, L. I., 209, 704
Aoi, G. K., 1047
Aoki, M., 906
Apgar, F. A., 675
Appel, E. G., 446
Applebey, M. P., 288, 603, 657
Appleyard, M. E. S., 448
Araki, T., 998, 1035
Aranda, V. G., 15
Arauz, J., 701, 1039
Arbidan, O. G., 651, 1116
Arbuzov, Yu. A., 87, 92, 93, 172, 421, 714
Arcadi, V. G., 1162
Archibald, F. M., 365, 396, 397, 398, 408, 443, 937, 1079
Ardagh, E. G. R., 490
Arditti, G., 907
Armendt, B. S., 839
Armistead, G., Jr., 134
Armour & Co., 731, 979
Armstrong, R. T., 15, 265, 1263
Armstrong Cork Co., 577
Arneil, A., 871
Arnold, J. C., 256
Aronov, S. G., 458
Arrias, E., 480
Artem'eva, O. A., 454, 1156
Artyunyan, S. S., 144, 171
Arup, P. S., 336, 381
Arveson, M. H., 1071
Asaoka, T., 502
Aschan, O., 1302
Ascherl, A., 728
Ashdown, A. A., 15, 265, 1263
Ashford, T. A., 628
Ashton, R., 318
Asipov, M., 1194
Askenasy, P., 254, 533
Asperen, van, 900
Asphalt Cold Mix (Australia) Pty. Ltd., 1217
Assman, K. S., 909
Associated Oil Co., 1064
Astin, S., 852
Aston, J. G., 568
Astrakhantzev, P., 745
Atal'yan, A., 23, 203, 209
Atkins, W. R. G., 1116
Atkinson, R. G., 210, 671
Atlantic Refining Co., 41, 44, 191, 470, 471, 477, 478, 486, 488, 489, 519, 659, 1044
Atlas Powder Co., 755
Atmospheric Nitrogen Corp., 279, 953, 1050
Atwell, H. V., 738, 929
Aubert, M., 1017, 1097
Auchy, C., 900
Audibert, E., 50, 352, 1225, 1234
Auerhahn, A., 171, 705
Auld, S. J. M., 37, 97, 885, 930, 932
Aurisicchio, G., 819
Austin, J. B., 260
Austin, W. E., 409, 813
Automotive Products Co., Ltd., 546

Auwers, K. v., 775
Avice, R., 1039
Axe, W. N., 583, 842
Ayers, G. W., Jr., 919, 928
Ayres, E., 215, 812, 917, 918, 919
Ayres, E. A., Jr., 801

B

Bachman, G. B., 146, 514, 565, 722, 824
Bachrach, D. J., 1114
Back, E. A., 566
Backer, H. J., 31, 471, 480, 505, 616, 678, 688, 689, 694, 696, 820
Backlund, N. O., 710
Backus, C., 1261
Backus, H., 21, 235, 251
Bacon, T. S., 461, 868, 1049
Baddeley, G., 96, 447
Baddiley, J., 1076
Badertscher, A. E., 732
Badger, E. B., & Sons Co., 380, 755, 801
Badische Anilin u. Soda Fabrik, 764
Badroux, F., 770, 775
Bachle, O., 172
Baehr, H., 458
Baeyer, A., 89, 763
Bagdassarjanz, O. S., 720
Bagirov, K., 1109
Bagley, G. D., 223
Bagnall-Bull, E., 731
Bahlke, W. H., 43, 46, 529, 1201, 1312, 1323
Bahr, T., 1242
Baidakova, R., 929
Bailar, J. C., Jr., 498
Bailey, C. F., 546
Bailey, J. H., 714
Bailey, J. R., 11, 832-834, 836-840
Bailey, K. C., 322
Baisse, J., 452
Bakelite Corp., 878
Baker, R. E., 528
Baker, W., 581
Bakshi, J. B., 273, 274
Balada, A., 1151
Balandin, A. A., 92, 173, 185, 257, 258, 302, 346, 880
Balas, F., 370
Balashov, E. F., 1192
Balázs, A., 747
Balcar, F. R., 283
Baldeschwieler, E. L., 1165, 1179
Baldwin, A. W., 487
Balls, A. K., 487
Baltimore Gas Engineering Corp., 1101
Bamford, C. H., 449, 450
Banc, M., 169, 278
Bandli, M., 251
Bank of Manhattan Co., 813
Banks, D. B., 45
Banks, F. R., 1019
Bannister, W. J., 919
Banse, H., 1279, 1280
Banús, A. G., 191
Barbaudy, J., 329
Barber, C. T., 22
Barber Asphalt Co., 1205, 1217, 1219
Barbier, H., 411, 416, 816
Barbosa, P. C., 933
Bardwell, D. C., 267
Barkhash, A. P., 897
Barmore, M., 1279, 1280, 1283, 1285, 1288
Barnard, D. P., 26, 930
Barnard, E. R., 930
Barnett, R. S., 1165
Baroni, A., 481, 482
Barr, F. T., 462
Barr, G., 1173, 1213
Barrett, E. G. V., 652
Barrett, H. J., 1120
Barrett Co., 486, 794
Barron, H., 252
Barsch, H., 1154
Barsky, G., 889
Bart, E., 929
Bart, E. V., 666
Bartell, F. E., 249
Barth, E. J., 756, 979
Bartkiewiczówna, J., 551
Bartlett, P. D., 514, 521, 531, 589
Barton, C. H., 1023
Barton, D. C., 17
Barton, P. D., 45
Bartram, J. G., 18
Bartram, T. W., 917, 918, 926
Basch, E., 576
Bashkirov, A. N., 144
Baski, J. B., 878
Bass, S. L., 405, 409
Bassett, H. N., 931
Basu, K. P., 765
Bataafsche Petroleum Maatschappij, 43, 44, 115, 158, 160, 163, 169, 175, 214, 224, 228, 241, 283, 292, 294, 300, 305, 308, 309, 323, 331, 358, 364, 389, 391, 392, 397, 409, 414, 417, 418, 420, 432, 433, 443, 444, 450, 451, 458, 475-477, 480, 489, 494, 509, 510, 516, 518, 520-523, 530, 531, 553, 567, 594, 607, 629, 670-672, 703, 705, 716, 719, 749-752, 978, 979, 1017, 1018, 1057, 1070, 1081, 1098, 1106, 1192, 1202, 1205, 1217
Batalin, V. S., 442, 509, 519, 520, 588
Batchelder, H. E., 672
Batchelor, H. B., 1202
Bateman, W. H., 24, 25, 26, 28
Bauer, A., 576
Bauer, A. D., 1165
Bauer, L. N., 581
Bauer, K., 557, 586, 715
Bauer, K. H., 201
Bauer, R., 562
Bauer, W., 527
Baum, E., 160, 430
Baumann, P., 170, 254, 255, 677, 710, 712
Baumann, W., 461
Baxter, J. P., 461, 716, 737
Bayer, O., 820
Bayerische Stickstoff-Werke A.-G., 244
Bayley, C. H., 60, 149, 150, 154, 171, 172, 178, 181, 182, 369, 375, 1035
Baylis, J. R., 252
Baylis, W. S., 667
Bazarova, D., 1078
Beale, E. B., 575
Beale, E. S. L., 1168, 1175
Beall, I. N., 14, 23, 24, 1337
Beamensderfer, J. S., 738
Beamer, C. M., 305, 365, 397, 408, 443
Beard, L. C., Jr., 577, 915, 917, 918, 926
Beard, R. E., 1071
Beattie, H. B., 989
Beattie, J. A., 14
Beatty, H. A., 198, 873, 874, 898
Beaver, D. J., 224
Beaulard, P., 367
Becher, C., Jr., 1016
Beck, C., 963, 974, 976, 977
Beck, H. V., 1170
Becker, A. E., 937, 1027
Becker, L., 417
Beckert, C. J., 373, 549
Beckwith, E. Q., 26
Beckwith, L. B., 1043, 1205, 1218
Bedos, P., 589
Beeck, O., 52, 56
Beek, P. A. A. van der, 922
Beekley, J. S., 279
Beeson, H. H., 890
Beest, A. C. van, 1176
Begetova, A. P., 650
Behncke, H., 519
Behre, C. H., Jr., 48
Behrens, F. B., 475
Behringer, K., 977
Beider, S., 935
Beilin, A. E., 669
Beilstein, F., 410
Beiswenger, G. A., 746
Beizel, N. M., 339
Bekht, I. R., 1161
Bekreneva, K. M., 1214
Belchetz, A., 475
Belchetz, L., 51, 52, 53, 55, 58, 61
Belikova, A., 307, 699
Bell, A., 804
Bell, J., 466, 896, 1010
Bell, R. P., 725
Bellas Processing Corp., 870
Beller, H., 971, 975, 976
Bencowitz, I., 1211
Bender, H., 781
Benedict, W. L., 455, 489, 914, 924, 927, 1043
Benedict, W. S., 273, 454
Benham, E. B., 1047
Bennett, C. T., 368
Bennett, H. T., 163, 529, 530, 577, 916, 917
Bennett, N., 782
Bennett-Clark Co., 475, 477
Bennett, Inc., 1217
Benning, A. F., 748
Benninghoff, W., 27
Benson, G., 701, 708
Bent, F. A., 282, 283, 288, 293
Bent, L. N., 578
Bentley, L., 1039
Bentley, W. H., 960
Beobide, J. G., 1035
Berchet, G. J., 687, 706, 708, 807
Bereslavsky, E. V., 1035
Bergel'son, A. B., 702
Berger, C. W., 1157
Berger, H. G., 217, 732
Berger, L. B., 466
Berger, P., 588
Bergman, G. G., 46
Bergmann, E., 649, 913
Bergs, H., 613
Bergstrom, F. W., 469, 787, 810
Berkenheim, A. M., 948
Berkovich, I. P., 828
Berl, E., 21, 1073, 1132
Berlin, K., 1027
Berlin, R. I., 972
Berliner, J. F. T., 374
Berliner, M., 494, 506
Bernard, H., 576
Berndt, W., 727
Berne-Allen, A., Jr., 38, 758
Bernhauer, K., 382, 401
Bernoulli, A. S., 532
Berry, A. G. V., 487, 1114
Berry, C. M., 589
Berry, T. M., 592
Bersworth, F. C., 497
Berthold, E., 790

Bertoni, G., 622
Bertonasco, E., 403
Bertram, E. A., 9
Bertsch, H., 309, 576, 1086
Bertsch, J. A., 783, 945, 960
Bespolov, N. E., 1150
Bestuzhev, M. A., 563
Bettini, S., 1039
Beute, A. E., 616, 820
Bewad, J., 1096
Bezzi, S., 482, 483
Bezzub, K. E., 556, 980
Bhagavantam, S., 1183
Bhatnagar, S. S., 367
Bhatt, C. T., 467, 720
Bibbins, E. E., 924
Bibikov, N. N., 730, 733
Bickmore, R. C., 914
Bidaud, A. F., 588
Bie, C. N. de, 149, 154
Biebesheimer, H., 21
Biedermann, A., 485
Biedermann, H., 168
Biehler, F., 1086
Biffen, F. M., 789
Bigelow, L. A., 792
Bignell, L. G. E., 22
Biilmann, E., 628
Bilger, E. M., 341
Billig, K., 16
Billings, E., 247
Biltz, H., 702
Biluchowski, Z. Z., 490
Bingham, E. C., 1173
Binnie, D., 168
Birch, C. A., 727
Birch, S. F., 42, 156, 171, 215, 417, 456, 533, 550, 646, 1018, 1165
Birchall, T., 996
Bircher, J. R., 263
Birckenbach, L., 629, 774
Bird, J. C., 1072, 1080
Birkhimer, E. R., 44, 453
Birmingham Electric Furnaces, Ltd., 1044
Birnbaum, K., 628
Bischoff, F., 350
Bitler, W. P., 967, 1053
Bittner, K., 825
Bjeregaard, A. P., 916, 918
Blacet, F. E., 1127, 1129
Black, C. K., 500, 543
Black, I. A., 260
Black, P. T., 519
Blackwood, A. J., 211, 674
Blade, O. C., 1160
Blagonravova, A. A., 1098
Blagovidov, I. F., 1103, 1105
Blair, C. M., 740
Blair, M. G., 1169
Blajot, B., 1149
Blech, W., 408
Blinova, A. M., 940
Bliss, R. H., 290, 1302
Bloch, A., 40, 988, 989, 992, 997, 1124
Bloch-Seé, 171
Blokh, O., 900
Blomfield, J., 1258, 1264
Bloomfield, G., 423, 443
Bloomfield, G. F., 627
Blott, J. F. T., 1214, 1217
Blount, A. L., 538, 543, 918, 1107
Bludworth, J. E., 863, 868, 1049
Blue, R. W., 1280
Blümich, E., 621
Blum, I. L., 1155
Blumenthal, R. E., 1267
Bluymin, I., 1192
Blyakher, Y., 111
Blythe, Wm., & Co., Ltd., 960
Blyudov, A. P., 1229, 1236, 1240
Boardman, C. C., 251
Boardman, D. W., 538
Bobinska, J., 1285
Bocharova, E. M., 878
Bockemüller, W., 774
Bodenstein, P. H., 468
Boe, E. S., 1211
Boeck, W., 1107
Boeckeler, B. C., 149
Boedecker, K., 1084
Böeseken, J., 463, 468, 480, 549, 695, 696, 876, 900
Boehm, E. F., 1258
Böhme, H. T., A.-G., 158, 309, 548, 1082, 1086, 1118
Böhme, R., 1118
Böhme Fettchemie G. m. b. H., 548, 576
Boehringer, C. F., & Soehne G. m. b. H., 717, 718, 728
Boehringer, C. H., Sohn, 1264
Boerlage, G. D., 1016, 1027, 1033, 1034
Bogan, J. B., 1266
Bogert, M. T., 649, 958
Bogdanova, O., 307, 699, 949
Boggs, C. R., 251
Bogoslovskaya, T. N., 258, 259, 261
Boguslavskii, I. M., 270
Bogwardt, E., 895
Bohdanowicz, C., 23
Boisselet, L., 935, 1168
Bollman, H. T., 95, 96
Bollman, M., 1039
Bolotin, A., 147
Bolt, C. C., 505
Bolton, E. R., 1164
Bolz, F., 535
Bond, G. R., Jr., 1158
Bond, H. A., 281, 742, 878, 879
Bone, W. A., 52, 845, 848, 871, 873, 896, 1010
Bonhoeffer, K. F., 50, 883
Bonnier, C., 354, 1023, 1030
Booher, J. E., 711
Boomer, E. H., 347, 348, 349
Boot's Pure Drug Co., Ltd., 810
Borden, E. G., 916
Borden, L. E., 476
Borghello, V. N., 807
Borglin, J. N., 466, 578
Borgman, Yu. A., 642, 643
Borgstrom, P., 1158
Borgwardt, E., 446, 550, 776
Borisov, A. E., 484
Borisov, P. P., 92, 111, 196
Born, G., 1094
Borsche, W., 767
Borst, W. B., 1058
Bosing, E. A., 475
Bost, R. W., 342, 463, 479, 484
Bottecchia, G., 728
Bottoms, R. R., 569, 573, 574
Bouckaert, J. J., 1264
Bouhuys, A. G., 1076
Boulanger, L., 135
Bourie, W., 1268
Bourne, W., 528, 1262
Bourquel, M., 1183
Bousquet, E. W., 822, 1059
Bovier, Z. S., 327
Bowden, E., 546
Bowen, A. R., 37, 202, 632, 671, 758, 1026, 1149, 1173
Bowen, E. J., 450
Bowlby, W. D., 759
Bowles, V. O., 283, 284, 1302, 1303
Bowman, P. I., 273
Bowman, S., 1184
Bowman, W. H., 490
Boyd, G. A., 1157
Boyd, J. H., Jr., 659
Boyd, T. A., 1012, 1019, 1023, 1024, 1030, 1098
Boye, E., 732
Boyle, C. L., 543
Bozhko, N. P., 253
Brachfeld, J. A., 574, 578
Bradford, B. W., 1000
Bradford, G. F., 1266
Bradt, W. E., 954
Brady, O. L., 425
Brailler, P. S., 730
Brame, J. S. S., 1149
Branchen, L. E., 507
Brand, J., 24
Brandes, O. L., 640
Brandt, P. I., 928
Branham, J. R., 1130, 1131
Bransky, D. V., 1081
Bransky, O. E., 1191
Brashnik, N. I., 1001
Brassert, H. A., 278
Brassert, H. A., & Co., 278
Bratton, A. C., 838, 840
Brauch, G. E. K., 826
Braudo, E. M., 1214
Brauen, W., 1195
Braun, G., 728
Braun, George, G. m. b. H., 1075
Braun, J. von, 12, 491, 726, 1103, 1104, 1109, 1110
Braune, A., 1229
Bray, U. B., 42, 43, 46, 529, 667, 710, 1043, 1201, 1205, 1218
Brazhnikov, V. T., 1105
Breakey, H. A., 98
Brearley, D., 806, 807
Breton, J., 980, 1006, 1010
Bretschneider, O., 737
Breuer, F. W., 729, 742
Brewer, A. K., 257
Brewster, R. Q., 1162
Brezinski, L. P., 307
Briand, M., 981
Bridgeman, O. C., 37, 911, 1035-1037, 1315
Bridgman, P. W., 367
Bridgwater, E. R., 672
Briggs, H., 20
Brik, A. N., 378
Brill, R., 712
Briner, E., 852, 887, 1000
Briscol, H. V. A., 720
British Celanese, Ltd., 161, 167, 323, 326, 359, 363, 364, 389, 434, 498, 542, 578, 581, 582, 818, 1112, 1113
British Dyestuffs Corp., 1076
British Industrial Solvents, Ltd., 340, 383, 403, 416, 427
British Thomson-Houston Co., Ltd., 759, 789, 812, 816, 941
Brittol Syndicate, Ltd., 1039
Britton, E. C., 418, 518, 550, 551, 605, 629, 749, 752, 783, 794, 798, 799, 894
Brizzolara, A. A., 1117
Broche, H., 1168
Brochet, A., 591, 598, 401
Brockman, C. J., 571
Brockway, L. O., 588
Brode, J., 946, 950, 951
Broderick, A. E., 369
Brodersen, K., 519, 558, 1076, 1078
Brodkorb, F., 274
Brodovich, A. I., 484, 1161
Broeze, J. J., 1033, 1034
Bronn, I., 170
Brookbank, E. B., 869, 1129
Brooks, A. E., 815

Brooks, B. T., 8, 9, 11, 17, 19, 20, 175, 298, 299, 305, 306, 309, 313, 314, 318-322, 325, 326, 345, 356-359, 361, 363, 364, 366, 369, 386-389, 391, 392, 394-396, 926, 1034, 1081
Brooks, D. B., 1030
Broom, W. E. J., 1026, 1173
Broun, A. S., 483, 1161
Brouwer, L. G., 306, 316
Brown, A. B., 43, 44, 529, 1081
Brown, B. K., 540
Brown, C. L. M., 354, 371, 538
Brown, E. S., 476
Brown, E. W., 565
Brown, G. G., 15, 102, 103, 142, 1002, 1030, 1033, 1169, 1318, 1320, 1322, 1323, 1333
Brown, L. T., 1037
Brown, R. H., 1165
Brown, R. L., 331, 1050
Brown, W. B., 556
Brown, W. E., 1256-1258, 1263
Brownlee, R. H., 221, 223, 241
Brownlie, D., 230
Bruce, E. L., Co., 790
Bruce, J., 761, 762, 763
Bruce, R. N. B. D., 489
Bruckner, S., 1151
Brück, O., 39
Brückner, H., 26, 27, 260, 466, 929, 992, 1170, 1224, 1225, 1240
Brumbaugh, J. D., 1257, 1261
Brunauer, S., 1280
Brunck, R., 1107
Brunner, H., 483
Brunstrum, L. C., 1079
Brus, G., 878
Bruson, H. A., 448, 605, 891
Brussov, J. J., 92
Brutzkus, M., 1012, 1149
Bruun, J. H., 14, 16, 942, 1131, 1195
Bruzac, J. F. A., 263, 669
Bryant, G. B., 433
Bryson, H. C., 1115
Bub, L., 636
Buc, H. E., 313, 365, 372, 378, 380, 397, 486, 604, 916, 1017, 1039, 1070, 1079, 1080
Bucci, F., 621
Buchel, J. A., 41
Buchheim, K., 782
Bucy, E. H., 755
Büchler, C. C., 43
Bueckert, H., 170, 255
Buell, A. E., 456, 477-480, 489, 1031
Bülow, H., 1129, 1242
Buffalo Electro Chemical Co., Inc., 475
Buffum, W. W., 1034
Buiko, G., 674
Buizov, B. V., 171, 172, 673, 674
Bukh, D. N., 1075
Bukreeva-Prozorovskaya, L. M., 175, 339
Bulavsky, G. L., 96
Bullard, E. F., 606
Bunte, K., 988, 989, 992, 997
Burch, H., 1261
Burda, N. I., 291
Burdine, T., 367
Burgeni, A., 171
Burger, P., 247
Burgess, C. F., Laboratories, Inc., 559
Burgess, M. J., 984, 1005
Burgin, J., 869
Burgin, J. H., 169
Burgoyne, J. H., 942
Burk, R. E., 95, 136, 470, 486, 659, 665, 915, 918, 1046
Burke, J. P., 408, 501
Burke, S. P., 862, 866, 874
Burmah Oil Co., Ltd., 1205
Burnett, R. F., 769
Burnin, P. L., 924
Burrage, L. J., 461, 652
Burrell, G. A., 21, 24, 1122
Burrows, G. H., 427
Burstin, H., 43, 1191
Burton, J. L., 1117
Burwell, A. W., 860, 962, 968-972, 1059, 1061
Bury, E., 319
Bushmakin, I. N., 520
Busi, M., 1259
Buss, H., 1094
Bussies, J. L., 927
Butkov, N. A., 103, 111, 143, 146, 178, 668, 936
Butkov, V. A., 116, 1033
Butler, T. A. V., 368
Butterow, A., 294
Bye, J., 628
Byrnes, C. P., 843, 850, 862, 863, 869, 880, 966, 967, 1053, 1056, 1060

C

C. & C. Developing Co., 263
Cabot, G. L., Inc., 247
Cabot, H., 1257
Cadenbach, G., 791
Cadenhead, A. F. G., 701, 708
Cadman, W. H., 159, 172, 182
Cady, G. H., 815
Caille, A., 319
Caine, A. M., 1265
Calamboy, A. B., 1039
Calco Chemical Co., 563
Calcott, W. S., 304, 708, 709, 748, 790, 829, 915, 917, 946
Calcutt, W. E., 322
Calder, D. S., 1096
Caldwell, B. P., 629
California Fruit Growers Exchange, 577
California Spray-Chemical Corp., 434, 1077
Calingaert, G., 15, 198, 824, 1160, 1165
Calloway, N. O., 811
Cambron, A., 60, 149, 150, 154, 171, 172, 178, 181, 182
Campa, A., 29, 34
Campbell, A. W., 220, 240, 810
Campbell, C. G., 198
Campbell, C. L., 755, 801
Campbell, J. M., 1019, 1024, 1030
Campbell, O. F., 230, 232
Campbell, S. E., 389, 833, 1107
Campbell, W. H., 1040
Canadian Electro Products Co., Ltd., 717
Canadian General Electric Co., Ltd., 941
Canadian Industries Ltd., 566, 626, 727, 728, 736, 743, 790, 822, 915, 916, 918, 1041
Canals, E., 755
Candea, C., 136, 137, 154, 155, 184, 196, 219, 227, 272, 855, 871, 874, 922, 923, 1016, 1102
Cannon, H. H., 476
Cannon, M. R., 36, 433, 1172
Cannon-Prutzman Treating Processes, Ltd., 476
Cantuniari, I. P., 90, 205, 1099, 1101, 1302
Capelle, G., 720
Carbide & Carbon Chemicals Corp., 171, 176, 300, 309, 319, 326, 327, 361, 379, 389, 392, 396, 434, 435, 441-443, 507, 528-530, 538-540, 544, 554, 558, 567, 568, 574, 575, 577, 578, 581, 586, 587, 595, 628, 704, 706, 716, 751, 808, 872, 878, 1049
Carbo-Norit-Union-Verwaltungs-G.m.b.H., 460, 919, 927, 929
Carburetted Gas, Inc., 1048
Carceller, J., 852, 1000
Card, S. T., 424
Cardarelli, E. J., 306, 420
Carey, W. C., 1213
Carius, L., 897
Carl, B. E., 198
Carl, R. W., 606
Carleton, P. W., 808
Carli, B., 570, 571, 1165
Carlisle, P. J., 281, 430, 710, 727, 728, 743, 916
Carlson, C. J., 1062
Carlson, E. W., 674, 1070
Carlson, G. H., 622
Carmody, W. H., 216
Carney, B. R., 457
Carney, S. C., 161, 397
Carothers, J. N., 192
Carothers, W. H., 89, 680-682, 687, 689, 705, 706, 708, 709, 763, 807, 823
Carpenter, C. B., 232
Carpenter, C. P., 733
Carpenter, D. C., 581
Carpenter, G. B., 446, 625, 698, 894, 1041, 1050
Carpenter, M. S., 496, 563
Carpenter, M. T., 163, 657
Carr, D. E., 46
Carre, P., 413
Carrier Engineering Corp., 738
Carrier, E. W., 976
Carrier, W. H., 738
Carrozzi, R., 918
Carruthers, J. E., 877
Carruthers, T. F., 300, 309, 326, 380, 544
Carson, S. C., 1101
Carsons, J. F., 902
Carter, A. S., 704-706, 709
Carter, J. B., 1256, 1257
Carter, P. L., 1114
Cary, J. S., 662
Casimer, E. E., 29, 1152
Caspe, S., 809
Cass, O. W., 208
Cassar, H. A., 370
Castiglioni, A., 907
Catlow, B., 960
Caudri, J. M., 214
Cauquil, G., 521
Cavel et Roegiers, 260, 261
Cawley, C. M., 483
Celanese Corp. of America, 422, 434, 542, 577, 818, 883, 889, 1112
Cerchez, V., 29, 30, 35
Chabley, E., 1161
Chadaeva, L. F., 1156
Chadeloid Chemical Co., 433
Chaffee, C. S., 369
Chaffette, M., 291, 1038
Chakravarty, K. M., 273, 274
Chaleil, M., 766
Chalk, L. J., 1190
Challenger, F., 485
Chalmers, W., 174, 632
Chamberlain, E. A. C., 992
Chamberlain, D. S., 1074
Chambers, T. S., 90
Chambers, V. J., 718
Chamot, E. M., 755
Champion, C. H., 247
Chandler, C., 787
Chaney, L. V., 467, 470, 477, 478, 480, 1158

Chang, W.-S., 828
Chapman, E., 1076
Chappell, M. L., 130, 213, 1046
Charitschkov, K. W., 1195
Charlot, G., 942
Charpentier, P., 452
Charrin, V., 22, 145
Chatfield, H. W., 1115
Chattaway, F. D., 1095
Chaux, R., 905, 907, 1014
Chavanne, G., 16, 711
Chayanov, N. A., 651
Chebotar, L. P., 919, 930, 940, 1044
Chechkina, O. M., 103
Chelintzev, G. V., 447, 565
Chemical Construction Corp., 223, 242, 464
Chemische Fabriken vorm. Weiler-ter Meer, 830
Chemische Fabrik Flörsheim H. Noerdlinger A.-G., 1214
Chemische Fabrik Griesheim Elektron, 465
Chemische Fabrik Pott & Co., G.m.b.H., 1070
Chemische Fabrik von Heyden A.-G., 782, 783
Chemische Fabrik vorm. Sandoz., 578, 1112
Chemische Forschungs-G.m.b.H., 340, 713
Cheney, M. H., 1259
Cheney Chemical Co., 1259
Cheng, S.-M., 136, 1035
Chernichkina, A., 1113
Chernov, G. I., 1161
Chernozhukov, N. I., 34, 855, 874, 930-932, 936, 937, 940, 1190
Cherntzov, S. M., 333, 421
Chernyak, P. V., 242
Chernyakovskaya, T. F., 701
Cherry, L. B., 263
Chesnokov, N., 674
Chesny, H. H., 189
Chester, A., 1266
Chevuichalova, K. K., 609, 706
Chicago Pneumatic Tool Co., 745
Chichibabin, A. E., 412, 416, 447, 563, 564, 605, 720
Chichonkin, M., 589
Chicos, I., 444, 1099
Chien, N.-C., 1035
Child, W. C., 1208
Chilingaryan, A. A., 346, 453
Chilton, T. H., 704
Chilvers, C., 1149
Chirvinskaya, E. Y., 879
Chistov, I. F., 442
Chittick, M. B., 212
Chiurdoglu, G., 16
Chmelevsky, A., 911, 1155
Chmielnicka, A., 469
Choudhury, S. C., 949
Chowdhury, J. K., 949
Christ, R. E., 904
Christen, C. C., 257
Christensen, B. E., 866, 1128
Christensen, C. W., 731
Christensen, L. M., 424, 1037
Christesco, 269
Christiansen, J. F., 1257
Christiansen, W. G., 335, 528
Christmann, F., 262, 671, 675
Chu, Y.-T., 1035
Chulkov, Ya. I., 729
Churakov, A., 558
Churbakov, A. M., 783
Church, J. M., 901
Chwala, A., 1074
Ciaravino, E., 733
Ciocca, B., 721
Ciochina, I., 669
Cioranescu, E., 90, 94, 185, 613
Claffey, L. W., 1195
Clapsadle, L. J., 539
Clar, E., 208
Clark, F. M., 789, 941
Clark, G. H., 727
Clark, L., 125
Clark, L. H., 390, 604, 751
Clark, R. H., 519, 804
Clarke, G. L., 1165
Clarke, L. A., 43, 44, 797, 801, 917
Clarkson, R. G., 785, 890, 915, 918
Classen, J. M. H. K., 701, 1040
Claxton, G., 916
Clayton, B., 575
Clement, J. K., 984
Clemo, G. R., 725, 901
Clerget, P., 1017, 1097
Cleveland Cliffs Iron Co., 342
Clifford, A. M., 464
Clifford, C. W., 1162
Coates, G. M., 529
Coats, H. B., 1176, 1187, 1318
Cochrane, E. W., 28
Cocking, T. T., 316
Cockram, C., 603, 657
Codier, O., 475
Coffex A.-G., 745
Coffey, S., 996
Coffman, D. D., 680, 709
Cogan, H. D., 616
Cohen, A., 619
Cohen, L. L., 992, 995
Cohn, H., 1241
Cohn, M., 1002
Colas Products Ltd., 1217
Cole, A. E., 471
Cole, H. A., 1145
Cole, P. J., 794
Coleman, G. H., 156, 307, 440, 499, 518, 551, 595, 716, 745, 749, 752, 798, 799
Coleman, J. D., 1012
Coleman, W. H., 1038
Colgate-Palmolive-Peet Co., 976
Collett, A. R., 527
Collier, H., 728
Collina, C., 1259
Collins, A. M., 680-682, 689, 706
Collins, J. O., 1208
Collins, R. G., 122
Columbia Engineering & Management Corp., 275, 276
Columbian Carbon Co., 240, 248
Comay, S., 490, 1157
Commercial Solvents Corp., 405, 409, 422, 423, 443, 541, 919
Compagnie de Bethune, 319, 327
Compagnie de produits chimiques et électrométallurgiques Alais, Froges & Camargue, 517, 711, 719, 745, 746, 830
Compagnie française pour l'exploitation des procédés Thomson-Houston, 941
Compagnie générale d'electricite, 728
Compagnie internationale pour la fabrication des essences et pétroles, 128, 129
Compagnie nationale de matières colorantes & manufactures de produits chimiques du Nord réunies, établissements Kuhlmann, 473
Conaway, R. F., 705
Concordia Bergbau-A.-G., 170, 190
Coninck, W. O. de, 720
Conine, R. C., 46
Conn, M. W., 479, 484
Connant, J. B., 1277
Connolly, A. G., 666
Connolly, E. E., 383, 416, 427
Connolly, G. C., 669
Connolly, J., 528
Connor, R., 340
Conover, C., 952, 958-960
Conrad, C., 909, 1038, 1168
Conrad, F. H., 1061
Conrad, R., 267
Consortium für elektrochem. Ind. G.m.b.H., 160, 342, 430, 436, 711, 714, 716, 811
Constable, E. W., 463
Conti, G., 22
Continental Oil Co., 111, 189
Conway, M. J., 24, 27
Conybeare, E. T., 1261
Cook, J. W., 619
Cook, L. W., 522, 797, 801
Cook, O. W., 718
Cook, R., 27
Cook, T. J., 529
Cooke, M. B., 654-657, 659, 661
Coons, A. B., 98
Cope, A. C., 500, 505
Corbett, A., 1034
Cords, M., 1168
Corell, M., 772
Coreth zu Coredo, A. P. A., 1039
Corey, C. H., 1199
Corlew, R. P., 979
Cornet-Cals, M. R., 424
Cornet-Cals, S., 424
Cornillot, A., 721
Cornish, R. E., 725
Corona Conversion Corp., 263
Correlli, R., 136
Corsinglia, J., 1006
Corson, B. B., 591, 596, 642, 654, 663, 664
Cosciug, T., 29, 31, 35, 36, 1104
Cottle, D. L., 588
Cotton, R. T., 376, 566
Cottrell, O. P., 42
Coulson, E. A., 40
Coustal, R. A., 1039
Coustolle, P. P., 576
Couture, J. R., 1214
Covert, L. W., 605
Coward, H. F., 983, 987, 989, 995, 1005
Cowles, H. C., Jr., 39, 477
Cox, A. W., 1170
Cox, D. C., 409
Cox, E. R., 14-16, 1138, 1314
Cox, H. L., 300, 309, 326, 336, 377, 529, 539, 544, 554, 577, 578
Cox, R. F. B., 427
Coxon, G. H., 161
Cragoe, C. S., 1176, 1325
Crahay, J. N., 433
Craig, R., 1070
Craig, W. A., 1205, 1214
Cramer, H. I., 346
Cramer, P. L., 1022
Crandal, E. E., 97-99, 133
Craven, E. C., 376, 424
Crawford, F. M., 423, 443
Crawford, J. W. C., 428, 451
Crebe, J. J., 783
Criegee, R., 52, 64, 895
Crima soc. anon., 331
Crippen, R. R., 1169
Cristescu, J., 112, 867, 1049
Cristodulo, N., 855, 874, 922, 923, 1016
Critchley, G. N., 35, 117, 119, 122, 135
Croco, C. W., 737, 811
Cromwell, N. H., 220, 240

Crone, H. G., 438
Croope, D. H., 302
Crosby, R. H., 457
Cross, P. C., 588
Cross, R., 1018
Cross, W. M., 1043, 1247
Crossley, F. S., 372, 889
Croxall, W. J., 308, 607, 609
Cruellas, J., 20, 47
Cryder, D. S., 32, 1225, 1303
Cuevas, N. L., 1039
Culbertson, J. B., 719
Cummings, H. K., 1029
Cunningham, O. D., 488
Cupery, M. E., 709
Curme, G. O., 808
Curtis, A. L., 781
Curwen, M. D., 1115

D

Dacheux, P., 910
Dackweiler, H., 932
Dadieu, A., 1183
Daeschner, C., 1188
Dahlen, M. A., 500, 543
Daimler, K., 1099, 1218
Dains, F. B., 1162
Dakin, M. A., 358
Dalfsen, J. van, 716
Dalin, M. A., 321, 323, 324, 326, 328
Damian, J., 932
Damien, M., 710
Damiens, A., 1124
Damon, E. H., 248
Dana, L. I., 539
Dănăilă, N., 30, 149, 154, 729, 1151
Danciger Oil & Refineries, Inc., 169
Danehy, J. P., 565, 722, 724
Daniels, A. C., 1279, 1285, 1288, 1289
Daniels, L. C., 789, 958-960
Danilina, M. I., 173
Danilov, S., 543
Danilovich, A. I., 968, 971
Danilovich, Z., 963
Dankova, T. F., 948
Danner, P. S., 1018
Dantsizen, C., 738
Darche, A., 1014
Darmois, E., 1177
Darrah, W. A., 1045
Das-Gupta, H. N., 721
Dashevskii, M. M., 955
Daudt, H. W., 304, 345, 735-737, 747, 792, 952
Daugherty, J. P., Jr., 115, 129
Daur, R., 1241
Davanakov, A. B., 972
Davenport, J. E., 1167
Davenport, R. H., 745
David, W. T., 1007
Davidsohn, I., 759
Davidsohn, J., 1117
Davidson, A., 820
Davidson, B. M., 1263
Davidson, D., 649, 958
Davidson, J. G., 595
Davies, I. W., 1000
Davies, J. A., 309, 389, 392, 396
Davies, R. M., 730
Davies, W. L., 708
Davies, W. R., 369, 375, 1035, 1185
Davis, A. P., 260
Davis, C. H., 1258
Davis, D. S., 535
Davis, G. H. B., 211, 215, 263, 278, 674, 758, 979, 1056, 1176, 1209
Davis, G. L., 427
Davis, H. M., 684
Davis, H. S., 385, 392, 1138
Davis, R. F., 488, 490
Davis, R. H., 704
Davis, W. N., 471, 488
Davis, W. S., 937
Davuidova, M., 709, 753, 801
Davuidova, N., 976
Day, A. R., 879
Day, J. E., 223, 244, 245
Day, R. B., 488, 490, 625, 668, 928
Dayton Synthetic Chemicals, Inc., 674
Dean, E. W., 1176, 1209
Deanesly, R. M., 162, 346, 390, 391, 393, 410, 417, 418, 509, 510, 749-751
Dearborn, R. J., 667
Debye, P., 1176
Decavel, 261
Deckert, W., 556
Deditius, L. F., 452
Dedusenko, L. S., 171
DeFazio, S. F., 1267
Degering, E. F., 336
Degiorgi, H., 728
De Groote, M., 577, 593, 1074, 1075, 1086, 1114, 1116
Degtyareva, A., 667, 914, 928
Deguide, H., 710
Dehn, W. H., 711
Dehnert, H., 458, 557
Deichmann-Gruebler, W., 681
Dei-Karkhanova, A. A., 1069
Delaby, R., 1151
Delaunois, A., 580
Delbridge, T. G., 1173
Deltombe, E., 56
Demchenko, A., 668
Dement'eva, M. I., 174, 357, 387, 744, 1142
Demole, E., 1094
Dem'yanov, N. Y., 620-622, 696, 762, 764, 1111
Dengler, F. S., 1205
Dénigès, G., 365, 372, 1093, 1094
Denisenko, Yu. I., 91
Dennemark, A. E., 1073
Denney, F. E., 519
Densham, H. B., 1261
DePree, L., 710
Derby, I. H., 232, 488
De Rewal, F. J., 953
DeRight, R. E., 505
Desai, P. G., 959
De Simo, M., 420, 450, 451, 548
Desreux, V., 753
Desseigne, G., 382, 401
Destrée & Cie., 465
Detoeuf, A., 515
Detwiler, J. G., 44
Deutsch, H., 713, 714
Deutsche Gasolin A.-G., 1107
Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler, 339, 343, 422, 423, 427, 430, 443, 713, 714, 717, 889
Deutsche Hydrierwerke A.-G., 453, 628, 820, 1086, 1120
Deutsche Vialit-Ges. m. b. H., 891
Deutsche Voltol Oel Gesellschaft. 261
Dewey & Almy Chemical Co., 248
Dianina, T., 963
Dickinson, A. G., 409
Dickinson, E. A., 666
Dickmann, H., 963, 974, 976, 977
Diegs, S. H., 434
Diels, O., 652, 688
Diependruck, O., 1073
Dietrich, K. R., 328, 330, 743, 1034, 1035, 1037, 1038, 1166, 1168
Dietrich, W., 964, 968, 971
Dietz, H. F., 1059
Dietzel, E., 758
Dietzler, A. J., 418, 818
Diggs, S. H., 43, 530
Dijk, J. A., van, 1150
Dillon, R. T., 1146
Dimitriu, M., 1152
Dintzes, A. I., 56, 58, 69, 70, 72, 102, 103, 1139
Dirsch, R., 626
Distilleries des Deux-Sevres, 406
Distillers Co. Ltd., 164, 175, 284, 285, 292, 294, 322
Dittrich, E., 236, 1156, 1162
Ditz, E., 89, 703
Diwoky, F. F., 43, 44, 255, 529, 1018
Dixon, E. S., 134
Dixon, H. B., 987, 989, 1000
Dixon, L. F., 566
Doak, G. O., 580
Dobromilskaya, I. M., 708
Dobrowolski, R., 490
Dobryanskii, A. F., 108, 109, 196, 458, 493, 494, 506, 753, 801, 1151, 1154
Dockendorff, R. L., 1173
Docksey, P., 1175, 1176
Docquier, P., 889
Dodds, E. M., 1006, 1027
Dode, M., 547, 557, 642
Dodge, B. F., 284, 288, 290, 574, 1302
Doeuvre, J., 901
Doherty Research Co., 241, 315, 356, 359, 365, 377, 396, 397, 408, 517, 862, 866, 874, 916, 928, 1081
Dohse, H., 431
Doladugin, A. I., 13, 23, 31, 33, 758
Dolbear, C. E., 670
Doldi, S., 1039
Dolgoplosk, B. A., 699
Dolgoploska, B. A., 880
Dolgopol'skii, I. M., 532, 546, 681, 797
Dolgov, B. N., 337, 338, 431, 878
Dolid, J., 577
Dolin, P. I., 164
Dominik, W., 551
Dominikiewicz, M., 888, 1067
Donaldson, R. N., 1192
Donath, E., 112
Dooley, M. D., 50, 53, 69
Doormaal, P. M. van, 1197, 1211
Doran, J. M., 319
Dornte, R. W., 932, 933, 936
Doroganyevskaya, E. A., 609
Doroshevskii, A. G., 367
Dorrer, E., 563
Dorris, T. B., 308, 376
Dorsett, W. C., 669
Dostal, H., 632
Doty, M. M., 97, 98, 133,
Dougherty, G., 468
Dougill, G., 459
Douglass, W. A., 946
Douthett, O. R., 1205, 1219
Dow Chemical Co., 156, 159, 191, 192, 194, 301, 307, 342, 407, 418, 499, 507, 518, 550, 551, 595, 605, 629, 710, 716, 730-732, 736, 745, 746, 749, 752, 778, 781, 783-786, 790, 794, 797-799, 818, 825, 894, 916

Dow, H. H., 194
Downing, F. B., 704-706, 708, 709, 785, 890, 915-918, 926
Downs, C. R., 861, 994
Doyarenko, M. N., 762
Doynel, I., 1034
Drägerwerk, H. und B. Dräger, 619
Dragan, A., 198
Drake, N. L., 400, 633, 755
Drake, W. V., 773
Dranitzina, U. A., 708
Draw, H. D. K., 619
Dreher, E., 648
Dreisbach, D., 580
Dressen, W. C., 732
Drewitt, J. G. N., 1095
Dreyfus, C., 434, 542, 577, 578, 818
Dreyfus, H., 149, 156, 158, 161, 166-168, 282, 287, 288, 291, 304, 305, 323, 326, 335, 358, 359, 422, 423, 516, 540, 542, 553, 559, 577, 579, 582, 589, 629, 712, 717, 745, 870, 878, 890, 893
Dribble, C. B., 507
Drinberg, A. Ya., 768, 1098, 1115
Drinkwater, J. M., 1015
Drogin, I., 219, 235, 236, 249, 250
Drosdoff, M., 464
Drossbach, O., 192, 950
Drozdov, N. S., 710, 954
Drozdov, S. S., 710, 954
Drury, D. R., 1256
Drushel, W. A., 325
Druzhinina, A. V., 1105
Dryakhlitzuina, V., 543
Dryer, C. G., 908, 913, 914, 918, 920, 922-924
Dubbs, C. P., 458
Dubbs, L. A., 112
Dubinin, B. M., 606
Du Bois, G., 329
Dubois, J., 77, 186
Dubois, P. F. D., 930
Dubrisay, R., 31, 1162
Dubrovai, K. K., 124, 135
Dubrovin, G., 242
Duchene, R., 1017, 1097
Duckert, R., 955
Dudenko, A. F., 909, 928
Dudley, J. F., 919
Duff, W., 231
Duffing, G., 1175
Dufraisse, C., 733, 855, 907, 1014
Duhring, E. L., 1117
Duimov, F. T., 346
Duimshitz, A., 1113
Dukiet, J., 1190
Dull, M. F., 423, 645
Dulou, R., 852, 895
Dumanois, P., 1014, 1029, 1034, 1038
Duncan, R. A., 1082, 1084
Dunlap, H. L., 370, 1172
Dunlop Rubber Co. Ltd., 439, 619, 829
Dunstan, A. E., 37, 179, 180, 184, 185, 478, 533, 631, 633, 634, 646, 654, 1189
Dunstan, W. R., 1096
Du Pont, G., 852, 895
Dupont, R., 907
Du Pont de Nemours, E. I., & Co., 159, 160, 169, 277-279, 281, 288, 304, 307, 316, 328, 340, 345, 362, 374, 393, 408, 420, 428, 430, 432, 433, 435, 438, 444, 446, 467, 472, 496, 500, 501, 528, 529, 533, 544, 546, 547, 551, 553, 560, 575, 576, 578, 581, 604, 611, 613, 614, 620, 622, 625, 626, 639, 641, 669, 678, 680-682, 685, 687, 689, 704-706, 708-710, 715, 727, 728, 742, 748, 755, 759, 785, 787, 792, 807, 808, 823, 825, 826, 829, 830, 851, 859, 871, 878, 879, 884, 891, 893, 894, 902, 903, 915-918, 949, 952, 957, 958, 1050, 1055, 1079, 1082, 1098, 1117, 1120, 1214, 1217, 1218, 1240
Du Pont Viscoloid Co., 540
Durand, J. F., 401, 409
Durgan, E. S., 1276
Durgin, C. B., 193
Durrans, T. H., 419, 800
Dusek, J., 242
Dvorak, J., 1037
D'yakova, M. K., 137
Dyck, W. J. D. van, 1016
Dykstra, F. J., 962, 972, 989
Dykstra, H. B., 705, 707
Dymock, J. B., 284-286, 292-294, 296, 340, 1302
Dyniewicz, H. .A, 1260
Dyson, G. M., 580
Dzioma, V. F., 540

E

Eagles, R. H., 249
Eastman, E. D., 1277, 1323
Eastman Kodak Co., 380, 415, 417, 496, 501, 507, 528, 588
Eastwood, R. A., 700
Eaton, G. L., 1311, 1316, 1323, 1325, 1327, 1331
Eatough, H., 1082
Ebaugh, I. A., 1116
Eberhardt, E., 708, 713
Eberhardt, R., 818
Ebert, G., 651
Eberz, W. F., 294, 296, 1303
Echols, L. S., Jr., 61, 555
Eckert, F., 1000
Edeleanu G.m.b.H., 42, 727, 739
Edgar, G., 873, 874, 898, 962, 972, 989, 1030, 1160, 1165
Edgcomb, L. J., 1128
Edlund, K. R., 305, 408, 414, 418, 544, 548, 589, 604, 606
Edminster, W. C., 1327, 1337
Edwards, A. M., 716
Edwards, D. F., 42
Edwards, H. D., 727
Edwards, K. B., 44
Edwards, M. W., 425
Edwards, W. R., Jr., 763, 765
Efremov, V., 1194
Efremova, E. M., 705
Egerton, A., 1013, 1015
Eggert, J., 1172
Egloff, G., 9, 28, 49, 50, 54, 56-58, 61, 62, 63, 65, 66, 74, 76, 78, 79, 81, 83-85, 88, 89, 95, 97-99, 104, 115-117, 133-135, 139, 142, 143, 146, 166, 187, 208, 213, 281, 454, 455, 478, 488, 490, 595, 614, 631, 632, 635-637, 645, 654, 657, 662-666, 668, 670, 703, 741, 861, 907, 908, 912-914, 919, 920, 922-924, 928, 929, 1017, 1028, 1034, 1035, 1038, 1044, 1045, 1199, 1307, 1310, 1316, 1323, 1329
Egorova, I. M., 13, 31, 33
Eguchi, T., 840, 841
Ehrhardt, U., 576
Ehrmann, K., 495
Eichler, T., 764
Eichwald, E., 43, 261
Eickmann, R., 1188, 1191
Eidus, Ya. T., 258
Eigeles, M. A., 1060
Eilers, L. K., 77, 79, 84, 87, 184
Eisenhut, A., 262, 1188, 1201
Eisenhut, O., 169, 225, 254, 255, 262
Eisenlohr, F., 16, 1177
Eisenmann, K., 525
Eisenstecken, F., 639
Eitner, P., 984
Elbe, G. von, 1005
Elbel, E., 479, 480, 487
Electric Metallurgical Co. of Canada, Ltd., 223
Electroblacks, Inc., 226, 244, 255
Electrolux, Ltd., 746
Electrolux Servel Corp., 539
Elektrische Glühlampenfabriken Kremenezky A.-G., 226
Elektronov, N. P., 271
Eliason, E. L., 529
Eliseeva, M. P., 34
Elley, H. W., 916
Elliot, A., 864
Ellis, Carleton, 7, 10, 17, 21, 22, 26, 29, 41, 46, 49, 50, 52, 55, 66, 81, 85, 88, 90, 95-97, 102, 103, 105, 115, 116, 119, 130-132, 138, 139, 146, 147, 165, 186, 215-217, 219, 220, 223, 224, 236, 240, 251-253, 261, 269, 282, 283, 293, 299, 305, 307, 319, 321-323, 356, 358, 364, 366, 386, 405, 406, 408, 414, 419, 427-429, 431-433, 437, 442, 443, 444, 453, 457, 462, 467, 471, 475, 479, 481, 483, 489, 491, 492, 495, 497, 499, 501, 503, 505, 507, 508, 510, 515-517, 520, 524, 529, 530, 532, 534, 535, 537-539, 541, 546, 548, 550, 557, 559, 562, 567, 575, 591, 596, 609, 614, 616, 617, 619, 628, 631, 632, 635, 647, 651, 652, 663, 667, 671, 673, 674, 676, 679, 680, 681, 683, 685, 688, 694, 696, 699, 701, 703, 704, 706, 709-712, 715, 717, 719, 726, 727, 733, 740, 741, 750, 755, 757, 760-763, 765, 767, 769, 775, 777, 778, 780, 782, 790, 794, 796, 800, 805, 808, 811, 815, 817, 818, 822, 823, 825, 829, 831, 834, 837, 839, 840, 842, 843, 845, 848, 864, 866, 871, 877, 881, 888, 890, 895, 907, 910, 912, 913, 922, 924, 930, 931, 933, 935, 945, 964, 965, 966, 970, 974, 977, 978, 980, 986, 1012, 1016, 1024, 1029, 1034, 1045-1047, 1058, 1064, 1065, 1069, 1080, 1086, 1090, 1099, 1101, 1102, 1104, 1109, 1111, 1113, 1120-1122, 1124, 1127, 1128, 1132, 1138, 1142, 1143, 1147, 1149, 1151-1154, 1156, 1157, 1169, 1170, 1189, 1201, 1202, 1209, 1217, 1223, 1243, 1244, 1246, 1247, 1253, 1255, 1278, 1298, 1302, 1303, 1307, 1311
Ellis, E. W., 475
Ellis-Foster Co., 406, 427, 828, 864, 890, 965, 966, 1045-1047, 1063
Ellsworth, D. C., 581
Elsmie, G. V., 425
Elsner, H., 537
Elteste, G., 1167
Emery Industries, Inc., 746, 1079
Empire Oil and Refining Co., 869, 872, 1049

Emschwiller, G., 711
Emsens, F., 135
Emulsoids Inc., 1112
Endo, E., 1017, 1030
Endo, H., 919
Endres, A. F., 476
Endres, R., 626
Engel, H., 197, 813
Engelder, C. J., 350
Engelke, E. F., 928
Englehard, J. W., 811
Engler, C., 17, 1161
Englin, B. A., 758
Engs, W., 161, 309, 386, 389, 390, 392, 394-396, 410, 635
Epidos soc. anon, 891
Epifanskii, P. F., 196
Epperson, E. R., 1172
Epprecht, A., 469
Erasmus, H. W. B. de W., 223
Erdheim, E., 669
Erdmann, E., 647
Eremeeva, O., 353
Eremin, E. N., 257
Erikh, V. N., 666
Erk, S., 1170
Erlenbach, M., 566
Erlenmeyer, E., 326
Erlenmeyer, H., 273
Erlikh, B. M., 1105, 1112
Ernotte, M., 1217
Ernst, O., 727
Ernst, P., 345, 742
Erskine, A. M., 1117
Ervin, H. O., 1160
Esch, W., 235
Eschenbach, W., 439
Eshevskaya, M. P., 102, 103
Esling, F., 1160
Espach, R H., 39, 1160
Este, 738
Estradere, S., 849
Estrovich, V. O., 981, 995
Eucken, A., 1139
Evans, C. C., 367
Evans, D. M., 669
Evans, E. A., 931, 1191
Evans, E. B., 907, 1026, 1027, 1034, 1179
Evans, E. I., 367
Evans, H. M., 549
Evans, R. A., 1040
Evans, R. N., 1167
Evans, S. M., 1267
Evans, T., 305, 414, 418, 544, 604, 606
Evans, W. M., 371
Evering, B. L., 50, 51
Evers, F., 257, 931
Eversole, U. H., 1266
Evstratov, V. F., 674
Ewald, G., 235
Ewing, F. J., 1109
Eymann, C., 169, 459
Eyring, H., 683

F

Faben, C. R., 232
Faber, W. F., 1042
Fabrication française de produits du lait, 501, 1039
Fabritziev, B., 674
Fachini, S., 930
Faerman, S., 783
Fain, J. M., 1219, 1220
Faingar, M. M., 935, 1214
Fairbourne, A., 1112
Fairley, A., 580
Fairlie, D. M., 1283
Fairlie, H. P., 1257
Fairlie, M., 935
Fakler, O., 434
Fam, F. M., 505, 824
Fano, E. da, 1220
Farady, M., 320
Faragher, W. F., 130, 636, 669
Farb- und Gerbstaffwerke Carl Flesh, Jr., 1112
Farmer, E. H., 627
Farrington, B. B., 469, 486
Fasce, E. V., 215, 595
Fassnacht, C. R., 728
Faucounau, L., 565
Faulconer, W. B. M., 1131
Faucutt, F., 728
Favorskaya, M. A., 682, 690, 698, 706
Favorskii, A. E., 511, 589, 690, 709, 721, 829
Fawcett, E. W., 313
Fayerweather, B. L., 916
Feder, E. A., 347
Fedorov, B. P., 83, 155, 172
Fedorov, S. F., 889
Fedoseev, P. N., 719
Fedotov, A. A., 1078
Fedotova, O. Y., 972
Feigin, A. B., 713
Feigin, A. L., 116, 1033
Feigl, F., 424
Feiler, P., 134, 158, 159, 160, 189, 892, 1017
Feinstein, J. M., 717
Feisst, W., 1125, 1224, 1234, 1237
Feist, F., 822
Felder, D. H., 1205
Felder, F. E., 1214
Feldman, J., 452
Feldman, M. H., 1257
Feldman, O., 1224, 1246, 1250, 1255
Felsing, W. A., 442
Fenn, H. N., 405, 409
Fenske, M. R., 32, 36, 334, 433, 1032, 1033, 1172-1174, 1176
Ferber, E., 702
Ferguson, C. V., 932, 933
Ferguson, G. E., 731
Ferguson, L. K., 529
Ferguson, R. H., 1081
Ferner, G. W., 370, 375
Ferreri, G., 1165
Ferrero, P., 56, 517, 533
Ferris, S. W., 39, 41, 44, 519, 1164
Fester, G. A., 20, 47, 253, 883
Fichter, F., 954
Fidelity Philadelphia Trust Co., 801
Field, E., 1076, 1184
Fields, J. D., 111, 929
Fieser, L. F., 687, 920, 1277
Fife, H. R., 41, 568, 574
Filippo, J. di, 253
Filyukova, A., 1112
Finckh, J., 483
Finger, G. C., 733
Finkel'shtein, V. S., 54, 227
Finlayson, D., 883
Finley, D., 1217
Finsterbusch, K. R., 657
Fiore, G., 1055
Firma Paul Lechler, 1219
Firma Stabilimenti di Rumianca, 730
Firsanova, E., 32, 34
Firth, J. B., 793, 957
Fischer, C., Jr., 1075
Fischer, E. J., 575
Fischer, F., 55, 73, 131, 155, 166, 168, 177, 214, 254, 814, 815, 1223, 1224, 1227-1234, 1236, 1237, 1239, 1241-1244, 1246-1250, 1252-1255, 1305
Fischer, F. G., 697
Fischer, G., 170
Fischer, G. M., 1115
Fischer, H., 1096
Fischer, H. G. M., 480, 918
Fishel, W. P., 824
Fisher, A., 133, 136, 232
Fisher, C. H., 957
Fisher, T. H., 566
Fishgold, H., 473
Fitch, L. H., Jr., 618, 1098
Fittig, R., 647
FitzSimons, O., 1172, 1175
Flach, J., 891
Flanzy, M., 878
Flavigny, B., 1215
Flavitzkii, F., 548
Flaxman, M. T., 758
Fleck, H. R., 572
Fleck, I. R., 1215
Flege, R. K., 293
Fleischer, J., 543, 738
Fleming, G. H., 754
Fleming, J. S. B., 330
Fleming, S. H., Jr., 370, 371
Flemming, W., 432, 450, 971
Flesch, C., 889
Flesch, H., 889
Fletcher, C. J. M., 554, 555, 884
Fletcher, W. A., 851
Flint, R. B., 496
Flintkote Corp., 1072, 1219
Flood, D. T., 198, 824
Flood, S. A., 715
Florentin, D., 572
Florez, L. de, 27, 669
Floyd, W. W., 11
Focsaner, O., 71, 72, 93
Foerster, F., 465
Fogelson, E. I., 1162
Fokin, S., 844
Folkens, K., 36
Follis, R. G., 457
Foohey, W. L., 500, 543
Forbes, G. S., 511
Ford, C. S., 1165
Ford, J. G., 940
Ford, T. F., 374
Ford-Moore, A. H., 580
Fordyce, C. R., 380, 588
Fordyce, R., 42
Foreman, M. O., 790
Formanek, J., 931, 1037, 1038, 1185
Forney, W. E., 123, 141, 144
Forrest, C. N., 1193
Forrest, H. O., 41, 133, 1201
Forst, W., 1132
Fortsch, A. R., 1325
Foss, B. Q. P., 133
Foster, A. L., 43, 151, 189, 230, 655, 662, 1034, 1035
Foster, H. B., 958
Foster, H. H., 1040
Fourneau, M. E., 767
Fowler, F. L., 519
Fox, A. C., 751
Fox, D. L., 832
Foy, E. M., 1032
Franceway, J. A., 263, 278
Franchetti, P., 224, 274, 276, 870, 938
Francis, A. W., 284, 291, 392, 1152, 1271, 1272, 1293-1296, 1298, 1302
Francis, C. K., 1058
Franck, H. H., 970
Francon, J., 551, 552
Franke, W., 711
Frantzuz, E., 1229, 1236
Franzen, H., 968, 975, 978
Frazier, R. B., 542
Frear, G. L., 880
Fredenhagen, K., 791
Frederick, D. S., 616
Frederik, G. H., 940
Free, G., 454
Freeman, C., 583
Freiman, G. M., 1145
Freitag, R., 789

French, H. E., 413, 799, 800, 803
Frenkel, G. A., 221, 249
Freund, E., 1096
Freund, M., 910
Frey, F. E., 50, 67-69, 89, 90, 93, 149, 160, 191, 268, 280, 601, 926, 1138, 1276, 1298
Freyermuth, G. H., 275, 278
Freytag, A., 698
Fricker, K., 569
Fridlyand, A. A., 1078
Fridman, S. G., 953
Fridshtein, I. L., 175
Fried, F., 228
Friedl, W., 30, 31, 1151
Friedmann, T. E., 354
Friedolsheim, A. v., 865, 971, 973
Friedwald, M., 631, 970, 1224, 1225, 1227, 1238, 1246, 1247, 1249-1251, 1255
Friend, F. A. C., 852
Friend, W. Z., 25, 26, 1101
Fries, F. A., 458, 651
Frigidaire Corp., 543, 733, 736, 737, 748
Fritzweiler, R., 328, 330, 1038
Frolich, P. K., 49, 59, 74, 76, 147, 149, 152, 160, 165, 179, 182, 219, 307, 314, 374, 435, 438, 472, 479, 611, 636, 659, 660, 727, 731, 758, 858, 860, 864, 867, 869, 874, 979, 1225, 1303
Frolova, P. A., 885
Fromin, V. A., 469
Frost, A. V., 54, 56, 58, 69, 72, 89, 167, 301
Frugnoni, O. B. von, 725
Fry, W. A., 9
Frydlender, J. H., 493, 726
Fryling, C. F., 862, 866, 874
Fuchino, K., 39
Fuchs, G. H. von, 44, 476
Fuchs, H. C., 539
Fuchs, N., 1169
Fuchs, O., 339, 430, 443
Fuchs, W., 1241
Fuel Development Corp., 1017
Fürst, K., 41
Fuidge, G. H., 1213
Fujiki, K., 745
Fujimoto, H., 882
Fujimura, K., 1227-1230, 1235, 1236, 1242-1244
Fujio, S., 89, 180
Fujise, S., 1096
Fukuda, Y., 245
Fuller, E. W., 486, 941
Fulmer, E. I., 424
Fulton, R. R., 546, 578
Fulton, S. C., 147, 625, 756, 814, 1082, 1189, 1190, 1192, 1208, 1214
Fulweiler, W. H., 807, 1177
Funduiler, B. M., 185, 722
Furihata, M., 756, 937, 1033
Furness, R., 970, 1112
Furumoto, H., 807
Furuya, H., 1030
Fuson, R. C., 207, 839, 1155
Fussteig, R., 39, 42, 99, 164, 324, 662, 1070, 1199

G

Gabel, Yu. O., 560, 589
Gabriel, C. L., 541
Gabriel, L. G., 1214, 1217
Gabrielyantz, S. M., 31, 32, 454, 1156
Gadaskina, N. D., 1151
Gaetz, H. T., 1187
Gagos, K. A., 1126
Gajendragad, N. G., 379
Gale, J. C., 823
Galibraikh, E. E., 54, 257
Gallagher, M., 343
Galle, E., 30, 31, 196, 1151, 1152
Gallo, G., 136
Gallsworthy, B., 469, 756, 978, 1056
Ganguli, S. K., 839
Ganguly, S. N., 686
Gans, D. M., 259
Gans, H. B., Jr., 529
Gaponenkov, T. K., 620
Garbsch, P., 651
Gard, E. W., 1204
Gardner, E. W., 1205, 1214
Gardner, F. T., 477
Gardner, J. B., 845, 848
Garelli, F., 571
Garfias, V. R., 10
Garlock, N. B., 442
Garner, F. H., 930, 1025-1027, 1034, 1173, 1192
Garner, J. B., 158
Garner, T. L., 249
Garner, V. E., 1006
Garofalo, R. J., 130, 433
Garratt, D. C., 368
Garton, E. L., 12
Garton, F. L., 1031
Garvan, F. P., 1034
Gary, W. W., 631, 1323, 1325, 1327
Gascard, A., 40
Gas Fuel Corp., 133
Gas Light & Coke Co., 459, 460, 489
Gasoline Antioxidant Co., 915-919, 926-928
Gasoline Products Co., 130, 161, 184, 1043
Gaubeau, J., 774
Gaucher, L. P., 15, 1325
Gaudion, G., 88, 645
Gault, H., 202
Gaus, W., 1018
Gauss, C. J., 1264
Gauvin, D., 647
Gavat, I., 612
Gaverdovskaya, M. V., 111, 196
Gavrian, P. le, 1221
Gavrilenko, E. S., 1162
Gavrilova, E. Y., 337, 339
Gay, N. N., 1079
Gay, W., 1037
Gayer, F. H., 307
Gebauer-Fuelnegg, E., 516, 560, 718
Gebhardt, O., 708
Gee, G., 632, 634
Gee, W. P., 433
Gehman, S. D., 249
Geiger, A. J., 711
Geigy A.-G., 1218
Geissler, M., 592
Geissler, W., 1213, 1220
Geissman, T. A., 214
Gelbke, M., 1074, 1105
Geller, L. W., 543
Gemant, A., 939, 940
General Aniline Works, Inc., 209, 527, 561, 575, 788, 810, 828, 957, 1083
General Atlas Carbon Co., 224
General Electric Co., 272, 738, 789, 941
General Motors Corp., 307, 733, 734, 736, 738, 748
General Motors Research Corp., 1098
General Petroleum Corp. of Calif., 1106
Generalov, V. M., 1150
Geniesse, J. C., 102, 105
Georgi, C. W., 539
Ger, M. P., 794
Gerbeth, F. L. de, 1054
Gerchikov, M. G., 405
Gerchikova, S. Yu., 234
Gerlach, R. G., 790
Gerling, E. K., 22, 1148
Germann, F. E. E., 567, 1126
Gerr, V., 323
Gerr, V. F., 110, 178, 909
Gerrish, H. C., 1040
Gervart, Yu. G., 666, 929
Geslin, M., 22
Gething, H. H., 957
Getz, C. A., 739
Geuther, 338
Gewerkschaft Kohlenbenzin, 114
Gewerkschaft Mathias Stinnes, 489
Gewerkschaft Victor, Stickstoffwerke, 1229
Gheorghin, D., 1001
Ghosh, J. C., 273, 274, 878, 1229
Giacomello, G., 852
Giauque, W. F., 1280, 1283, 1285
Gibbs, H. D., 861
Giberton, A., 466
Gibson, G. E., 1277, 1279, 1285
Gibson, R. O., 313
Gieb, K. H., 849
Gieseler, K., 1097
Gifford, H. W. F., 112
Gilbert, C. L., 1184
Gildersleeve, S. P., 374
Giles, R. N., 46
Gilkey, W. A., 787
Gill, A. E., 529
Gill, S., 8
Gillespie, B., 725
Gillet, A., 1229
Gilliland, E. R., 283, 284, 1302, 1322
Gillis, E. R., 1160
Gillis, J., 580
Gilman, H., 824
Gimmel'man, G. A., 1001
Ginsburg, J. M., 519
Ginzburg, A. A., 705
Ginzburg, E., 103, 145
Ginzburg, R. I., 23
Giordani, C., 130
Giordani, M., 726
Girdler Corp., 569, 573, 574
Givaudan, L., & Cie. Soc. anon., 794, 877
Givaudan-Delawanna, Inc., 496, 563, 605
Givaudon, J., 910, 911, 1176, 1177
Gladstone, M. M., 317, 318
Glasebrook, A. L., 51, 201
Glasplakatefabrik Union G.m.b.H., 1174
Glaxner, H. J., 248
Glazebrook, H. H., 450
Glazunov, G. I., 674
Gleason, A. H., 441
Glidden Co., 1217
Glizmaneko, D. L., 254
Globov, V. A., 165
Glockler, G., 257
Gluesenkamp, E. W., 750
Gluizdenok, V. M., 909
Gluud, W., 274
Gobert, 131, 254
Godbole, N. N., 629
Godchot, M., 520, 521, 764
Godlewicz, M., 45
Goettsch, G., 1150
Goetze, K., 461, 974
Gofferjé, E., 758, 828
Goheen, G. E., 440

Gohr, E. J., 1298
Goldberg, D., 495, 1104, 1109
Goldberg, E., 778
Golde, R. H., 940
Goldman, J. L., 1258
Gol'dman, M. M., 520
Goldovskii, B., 964
Goldsby, A. R., 86
Goldschmidt, H., 401
Goldschmidt, S., 528, 626
Goldstern, W., 1325
Golendeev, V. P., 963
Gollmar, H. A., 458, 459
Golubev, V. V., 23
Golubovskaya, N., 334
Gomberg, M., 519
Goodman, L. S., 711
Goodrich, B. F., Co., 429, 810
Goodwin, L. F., 424
Goodwin, N., 246
Goodyear, G. H., 86
Goodyear Tire & Rubber Co., 497
Gordon, K., 1035
Gorham, A. P., 727
Gorin, Yu. A., 173, 389
Goritzkaya, O. V., 1077
Gorn, A., 1125
Gorn, I. K., 347
Gorniak, J., 73
Gorskii, A., 772, 775
Gorsuch, E. H., 1078
Goryainova, N. S., 335
Gosudarstvennoe Ob'edinenie Azerbaidzhanskoi Neftyanoi Promuishlemnosti "Asneft," 1073
Goswami, H. C., 431
Gotovtzev, 1069
Goubeau, J., 629
Gould, E., 1078
Goulden, H. D., 1263
Goulding, E., 1096
Govakov, V. P., 142, 908
Govers, F. X., 43, 44, 130, 379, 433, 434, 574
Graefe, E., 1161, 1214, 1215
Graefe, E. H. E., 1224, 1255
Graenacher, C., 787, 977
Graham, G. L., 733
Graham, R. N., 327
Graham, R. P., 1063
Gramenitzkii, N. D., 935
Grandone, P., 180
Granger, R., 520
Grant, D. H., 1078
Grasselli Chemical Co., 380, 465, 576, 1041, 1059
Grassman, H., 1166
Graul, O., 1094
Graves, G. D., 39, 159, 304, 435, 438, 444
Graves, M., 379, 382, 401
Gray Processes Corp., 478, 479, 666, 667, 926, 928, 929
Gray, R. B., 1037
Gray, T. T., 479, 666, 667, 928
Great Western Electro-Chemical Co., 781, 1096
Grebe, J. J., 156, 732, 746
Green, S. J., 889
Greenberg, J., 435, 438, 440
Greene, E. S., 415
Greenewalt, C. H., 435
Greenfield, E. W., 1180
Greenfield, S. N., 1115
Greengard, H., 770
Greensfelder, B. S., 44
Greenstreet, C. J., 189, 1039
Greer, P. S., 336, 377, 538, 554, 578
Gregg, S. J., 1172
Gregory, A. Y., 731
Gregory, L. B., 574
Gregory, L. S., 477
Gregory, T. B., 408
Greig, M. E., 541
Greiner, E. E., 1176
Grevel, A., 1098
Gribova, E. I., 674
Griendt, G. H. van de, 389, 417
Griffin, R. C., 1161
Griffith, A. A., 938, 1037
Griffith, F. E., 1205, 1214
Griffith, H. R., 1266
Griffith, R. H., 70, 489, 944, 1098, 1179
Grignard, V., 601, 772
Grigor'ev, V. M., 779, 782
Grigorov, S., 242
Grimm, H., 698
Grimme, W., 169, 170, 214
Gröbner, W., 1125
Groggins, P. H., 448, 786, 789
Groll, H. P. A., 169, 178, 182, 184, 186, 187, 444, 476, 522, 523, 716, 889, 929
Groombridge, W. H., 161, 167, 326, 359, 363, 364, 389, 422
Gross, H. H., 43, 433, 453, 488
Gross, M., 1039
Gross, P., 580
Gross, P. M., 566
Grosse, A. V., 199, 200, 202, 595, 596, 598, 599, 602, 1301
Grosse-Oetringhaus, H., 1153
Grossman, F., 1038
Grote, W., 41, 42, 1163
Grote, W. H., 248, 249
Gruber, W., 728
Gruning, A., 710
Gruse, W. A., 40, 301, 488, 495, 604, 640, 929, 930
Gschaider, B., 251
Guest, H. H., 724
Guest, H. P., 720
Guha, P. C., 839
Guida, H., 38
Guillemonat, A., 852, 900
Guinot, H. M., 339, 427
Guiteras, J., 191
Gukhman, L., 209, 667, 928
Gulf Oil Corp., 604, 929
Gulf Oil Corp. of Pa., 930
Gulf Refining Co., 197, 215, 301, 488, 604, 812, 917-919, 929, 930
Gulf Research & Development Corp., 495
Gulkovskii, P. A., 1115
Gunness, R. C., 283, 284, 1302, 1303
Gurevich, Z. B., 879
Guruindin, K. S., 143
Gurvich, G. B., 1107
Gurwitsch, L., 28, 1117
Gusev, N. N., 1009
Guseva, A. R., 565, 823
Gustafson, C., 721
Gustafson, C. E., 918
Gustavson, G., 207, 602
Gustus, E. L., 611
Gutehoffungshütte Oberhausen A.-G., 264, 872, 881-883, 903
Guthrie, 621
Guthrie, B., 933
Gutner, R. A., 493, 506, 783
Gutt, J., 775
Gutuirya, V. S., 321, 323, 324, 326, 328, 358, 1090
Gutzait, A. M., 930
Gutzeit, C. L., 840
Guyer, J. A., 240, 280, 661
Gwathmey, J. T., 1257

H

Haardt & Co., A.-G., 579
Haas, J., 702
Haber, F., 50, 101
Hachmuth, K., 1169
Hachtel, F., 299, 321, 322
Hadler, B. C., 749, 752
Hadley, D. J., 439
Hadlock, C., 14
Häffner, F., 698
Hähle, H., 1115
Häuber, F., 172
Haeuber, H., 55, 78, 115, 158-160, 171, 189, 214, 263, 639, 665
Haffner, A. E., 896
Hager, F. D., 434
Hager, J. J., 220, 240
Haggard, W. H., 1256
Haggott, W. A., 1098
Hague, C. W., 1062
Hague, E. N., 156, 171, 179, 180, 184, 185, 187, 631, 646, 654
Hahn, C. A., 929
Hailes, R. G., 781
Haines, L. B., 621
Haitinger, L., 622
Haldeman, W. S., 1052
Hale, W. S., 487, 783, 784, 786, 794, 797, 1050, 1052
Halferdahl, A. C., 1323
Hall, C. P., 577
Hall, F. C., 41, 256, 261, 671
Hall, H. J., 146, 514
Hall, O., 540
Hall, W. K., 466
Hall Tobacco Chemical Co., 566
Haller, R., 577
Haller, W., 278
Halliwell, F. B., 27
Halloran, R. A., 213
Hal'pern, G. D., 700
Halpern, M., 636, 666
Halsey, J. T., 1263
Halvorsen, A. L., 1218
Hamai, S., 501, 742
Hambsch, O., 578
Hamilton, W. G., 457
Hammar, H. E., 19
Hammell, R. H., 126
Hammer, B. W., 708
Hammerich, T., 1035
Hammerschmidt, E. G., 27
Hammond, P. D., 468
Hamor, W. A., 1170
Hampton, B. L., 583
Hampton, W. H., 486, 488
Handovsky, H., 434
Hands, C. H. G., 1176
Hanks, W. V., 275, 276, 278
Hanlon-Buchanan, Inc., 863, 868, 890, 1049
Hannum, C. W., 315, 317, 318, 716, 916
Hanseatische-Mühlenwerke A.-G., 915
Hanson, V. F., 226
Hantzch, A., 1093, 1094, 1096
Happel, J., 469
Harbone, R. S., 1113
Harder, M., 964, 967, 971, 976
Hardy, D. V. N., 339, 380, 407, 626, 1050
Hardy, W. B., 1149
Harford, C. G., 627
Harger, J., 864
Hargraves, R. E., 227
Haringhuizen, P. J., 939
Harkins, W. D., 259
Harnsberger, A. E., 189
Harrell, J. W., 1325
Harrington, E. R., 22

Harris, B. R., 373, 545, 546, 549
Harris, C. R., 281, 710, 727, 743, 916
Harris, E. J., 1175
Harris, J. M., 1044
Harris, L., 15, 265
Harris, L. E., 375
Harris, P. L., 318, 723
Harrison, J. B., 485
Harrison, J. W., 126
Harry, R. G., 745
Hart, E. J., 777
Harteck, P., 849, 883
Harter, H., 278, 881
Hartman, W. W., 417, 507, 527
Hartmann, A. N., 1173
Hartmann, H., 595
Hartmann, M., 809
Hartner-Seberich, R., 1253
Hartung, W. H., 372, 889
Hartwell, F. J., 983
Harvey, N. D., Jr., 575
Harwood, J., 979, 1000
Hasche, R. L., 885
Hase, A., 556
Hase, R., 1185
Hasenbach, W., 465
Haskin, C. P., 933
Haslam, R. T., 132
Hass, H. B., 586, 588, 740, 750, 752-754, 766, 806, 1087, 1093, 1097, 1098, 1101
Hassenbach, H., 1171
Haswell, C. H., 1220
Hatcher, W. H., 334, 897
Hauck, B., 731
Hauck, F., 1154
Hauptmann, H., 510
Hautzsch, A., 620
Hawkins, K. S., 902
Hay, S., 182
Hayden, O. M., 709
Haylett, R. E., 530, 1201
Haymann, D. F., 1127
Hayward, W. A., 1176
Head, F. S. H., 619
Headington, C. E., 1171, 1177
Headlee, A. J. W., 527
Heany, N. S., 1257
Heard, J. R., 953
Hearne, G., 476, 510, 522, 523, 716
Heberlein, E., 483
Hebl, L. E., 1031
Hechenbleikner, I., 464, 827
Heckel, H., 1079
Heckel, W., 903
Heckert, H. W., 554, 555
Heckt, F., 540
Heid, J. B., 241
Heiman, S., 102
Heindel, R. L., Jr., 193
Heiningen, J. van, 985
Heinrich, F., 1125
Heinze, R., 654, 1030, 1155, 1161
Heise, R., 208
Heisig, G. B., 267, 683, 684
Heitmann, M. J., 1220
Hell, C., 511, 513
Heller, A., 533
Hellthaler, T., 973, 1057
Helmore, W., 915, 938, 1037, 1097
Hel'ms, I. E., 339
Helwich, L. A., 1034
Hemilian, W., 819
Hemptinne, A. de, 261
Henderson, J., 20
Henderson, L. M., 39, 44, 477
Henderson, V. E., 1256, 1257, 1263, 1265, 1266
Hendrey, W. B., 1107, 1108, 1110, 1114, 1116
Hendrixson, P., 345
Henke, C. O., 444
Henkel & Co. G.m.b.H., 406, 479, 480, 487, 526, 543, 566, 822, 829, 1082, 1083, 1116, 1120
Henle, F., 342
Henne, A. L., 733, 734, 736, 737, 748, 749
Hennell, H., 320
Hennicke, W., 227, 275, 278
Hennion, G. F., 384, 403, 406, 706, 722-724
Henriksen, A., 758
Henry, I. W., 267, 268
Henry, L., 520, 587, 1095
Henson, D. D., 842
Henstock, H., 330
Henze, H. P., 740
Hepburn, D. McK., 1216
Hepp, H. J., 67-69, 601
Herbert, T. M., 728
Herbert, W., 636
Herbig, W., 1076
Herbrich, J., 1035, 1185
Herbsman, A. M., 757
Herbst, H., 112
Hercules Powder Co., 46, 466, 519, 538, 539, 543, 578, 759
Herglotz, F., 1241
Herlinger, E., 913
Hermejo, L., 1159
Herndon, J. M., 400, 759
Herold, J., 720
Herold, P., 461, 497, 614
Herrara, J. J., 471, 1159
Herrenschmidt, J. D., 1179
Herrman, A., Ltd., 1214
Herrman, M., 645
Herrmann, J., 1129
Herrmann, W. O., 160, 340, 430, 713, 714
Hershberg, E. B., 687
Herstad, O., 1169
Herstein, B., 320
Herthel, E. C., 353, 928
Herzenberg, J., 490, 1043
Herzfeld, K. F., 51
Herzog, R. O., 171
Hess, F. G., 604
Hess, L., 745
Hess, R. W., 486, 487
Hessle, E. T., 467, 1077, 1080
Hester, W. F., 604, 605
Hetzel, T. B., 1033, 1034
Heublyum, R., 977
Heusler, F., 1161
Hey, D. H., 957
Heymans, C., 434, 1264
Heyne, G., 815
Hibben, J. H., 32, 1181, 1183
Hibbert, H., 341, 443, 541, 544, 715
Hibou, J. B., 1106
Hickinbottom, W. J., 614, 615, 691
Hickman, T. M., 1219
Hicks, J. A., 1170
Hicks-Bruun, M. M., 14, 16
Hieber, W., 535, 570
Hiedemann, E., 259
Hiers, G. S., 771
Higgins, E. C., Jr., 477
Higgins, E. J., 1080
Higgins, R., 933
Hightower, J. V., 43
Hilbert, G. E., 615
Hildebrand, J. H., 1325
Hildisch, D., 577
Hill, A., 565
Hill, A. E., 1158
Hill, A. J., 722
Hill, C. W., 1220
Hill, H. S., 715
Hill, J. B., 9, 28, 44, 667, 928, 1030, 1176, 1187
Hill, S. G., 873, 944, 1098
Hilliger, B., 1149
Hilliker, W. P., 1079
Hillis, D. M., 267
Hillman, E. S., 925
Hinckley, J. A., Jr., 317
Hindin, L., 907
Hinds, G. E., 750
Hinegardner, W. S., 884
Hinonishi, S., 54, 167, 180
Hinshelwood, C. N., 427, 554, 884
Hintermaier, A., 1116
Hinton, H. D., 383, 384, 406, 603, 604
Hintzmann, K., 1073
Hinz, G., 540
Hirata, F., 1175
Hirota, K., 725
Hirsch, E., 275
Hirsch, J. H., 120
Hirschberg, G., 189
Hirst, L. L., 573
Hjerpe, E. B., 301, 495
Hladky, J. W., 15
Hobart, F. B., 130
Hochschwender, K., 764
Hock, H., 898, 905, 906
Hock, L., 245, 261
Hodge, E. B., 1087, 1093, 1097, 1098
Hodson, G. C., 738
Hodson, W. D., 496, 576
Hoelzer, 464
Höppler, F., 1175
Hoess, W., 679, 930
Hofeditz, W., 50
Hoff, A., 628
Hoff, R. W., 354
Hoffer, M., 889
Hoffert, W. H., 910, 913, 916
Hoffmann, E., 1094
Hofmann, A. W., 877
Hofmann, F., 758, 1027, 1097
Hofmann, H. E., 453
Hofmann, K. A., 702
Hofmann, L., 605
Hofmann, U., 174, 252, 586
Hofmeier, H., 621, 1155
Hofsäsz, M., 629, 657, 703
Hoftman, M. V., 458
Hogness, T. R., 50
Holde, D., 1111, 1164, 1173, 1188, 1191, 1192, 1254
Holland, W. W., 122
Holleman, A. F., 1092
Holleman, M., 1095
Hollings, H., 182, 456, 460, 489, 1179
Holloway, T. B., 529
Holm, M. M., 26, 283, 291, 362, 396, 471
Holmberg, B., 481
Holmes, A., 1208
Holmes, H. N., 348, 783
Holmes, J., 371
Holowchak, J., 568
Holsen, F. F., 194
Holt, H. S., 467, 546
Holt, L. C., 345, 733, 735, 736
Holthaus, C., 1162
Holton, A. B., 529
Holzman, E., 1070
Holzverkohlungs-Industrie A.-G., 329
Homeyer, A. H., 318, 400, 895
Honen Seiyu, K. K., 710
Honig, P., 1167
Hooker Electrochemical Co., 324, 326, 327
Hoots, H. W., 8
Hoover, C. O., 477
Hoover, G. R., 1205

Hoover, K. H., 544
Hope, E., 773, 775
Hopff, H., 444, 445, 563, 794, 1099
Hopkins, B. S., 370
Hopkins, C. Y., 369, 375, 1034, 1035
Hopkins, G. R., 21, 28, 98, 235, 251
Hopkins, M. B., 404
Hoppel, J., 1139
Hopper, B., 1201
Horak, J. J., 576
Horclois, R., 676, 679
Horie, F., 33, 35, 454
Horiuchi, J., 260
Horn, C. L., 756
Horn, E., 826, 827
Horn, O., 1240, 1251
Horn, W. R., 288
Horning, H. L., 1023
Horsfall, W. R., 556
Horsley, G. F., 163, 164, 186, 287, 293, 788
Horst, D. T. J. ter, 939, 940
Horton, A. T., 450
Horwood, J. F., 897
Houdry, E. J., 126-130, 636, 669
Houdry Process Corp., 115, 126-130, 636, 669
Hough, A., 546
Houghton, R. E., 425
Houghton, W. F., 41
Hovorka, F., 580
Howard, F. A., 374, 674, 915
Howard, H., 465
Howard, J. L., 256, 261
Howard, J. W., 828
Howe, L. I., 549
Howes, D. A., 633, 634, 646, 654, 1034, 1035, 1149
Howes, R. T., 1204
Hoyer, H., 628
Hoyt, L. F., 930
Hsieh, T. Y., 383, 402, 412
Hsu, M., 770
Hu, M., 770
Huang, H. T., 729
Hubbard, P., 1202, 1213
Hubbuch, L. P., 496
Hubendick, E., 1149
Huber, J. M., Corp., 249
Hubert, O. A., 353
Hubner, W. H., 1029
Hueper, W. C., 538
Huettner, R., 272
Huff, H. F., 1030
Huffman, H. M., 101, 1225, 1271, 1274, 1276-1286, 1288-1297, 1302-1304
Huffmann, J. R., 426, 472
Hugel, G., 827, 1152, 1224
Huggett, J. L., 42
Huggins, K. A., 686
Hughes, A. C., 1213
Hughes, E. C., 470, 1046
Hughes, E. D., 378, 412, 797-799
Hughes, E. M., 1114
Hujio, S., 169
Hulsart, C. A., 193
Hulst, T. J. N. van der, 1177
Hulster, J., de, 643
Hultman, E W., 488, 853
Hultman, G. H., 458
Hultman and Powell Corp., 488, 853
Hummel, S., 22
Humphrey, I. W., 46, 539
Humphreys, R. L., 469, 486
Hund, W. L., 577
Hunt, M., 617
Hunt, S. B., 895
Hunter, L., 531, 1092
Hunter, T. G., 758
Huntington, R. L., 102
Huppke, W. F., 149, 280, 1276, 1298
Hurd, C. D., 51, 62, 63, 69, 74, 77, 79, 84, 86-88, 96, 171, 184, 423, 438, 442, 904
Huscher, M. E., 302, 629, 716, 752, 894
Huston, R. C., 383, 402, 412, 416
Hutchison, W. K., 456, 459, 460
Hutton, D., 704, 706
Huyser, H. W., 390
Hyams, F. C., 316
Hydraulic Brake Co., 539, 540
Hydrocarbon Converter Co., 1047
Hydrocarbon Processes, Inc., 112
Hyman, J., 675, 928, 1059

I

Ibing, G., 1245, 1253, 1254
Ichikawa, Y., 1199
I. G. Farbenind. A.-G., 55, 78, 95, 112, 114, 115, 134, 158-160, 161, 169-172, 174, 175, 185, 186, 189, 190, 192, 193, 204, 209, 210, 212-216, 225, 227, 228, 242, 249, 254, 255, 262, 263, 272, 275, 278, 281, 301, 304, 307, 311, 329, 331, 345, 347, 353, 365, 378, 406, 409, 427-429, 431, 432, 434, 450, 458, 461, 464, 465, 472, 479, 480, 486, 487, 495, 497, 499, 507, 519, 524-527, 539, 543, 557, 558, 560-564, 566, 569-572, 574, 576, 578, 579, 586, 587, 590, 594-596, 609, 618, 634-636, 639, 642, 651, 665, 671, 672, 674, 675, 677, 679, 680, 682, 688, 690, 698, 705, 708, 710, 712, 713, 715-719, 721, 727-729, 732, 742, 743, 745, 746, 748, 758, 759, 768, 772, 788-790, 794, 805, 810, 813, 817, 819, 820, 822, 828, 865, 889, 892, 893, 913, 914, 918, 928, 929, 944, 946, 950, 951, 953, 955, 956, 963, 964, 967-979, 1017, 1018, 1039-1041, 1054-1057, 1061, 1073, 1076-1078, 1086, 1099, 1115, 1153, 1188, 1201, 1218, 1228, 1244, 1252, 1255
Igawa, S., 1229, 1235, 1236
Ignatovskaya, I. Iz., 935
Ignatyuk, V. A., 651, 673
Illing, V. C., 19
Immendorff, H., 208
Imperial Chemical Industries, Ltd., 163, 164, 168, 186, 287, 288, 293, 330, 359, 421, 428, 451, 486, 487, 559, 562, 566, 569, 603, 657, 681, 710, 711, 715, 716, 737, 781, 782, 820, 853, 895, 1076, 1097, 1098
Indian Refining Co., 43, 44, 130, 379, 433, 434, 574
Industrial Patents, Ltd., 757
Ingold, C. K., 378, 503, 508
International Bitumen Emulsions Corp., 1218, 1220
International Hydrogenation Patents Co., Ltd., 538, 576, 642, 914, 930, 1192, 1201
Iol'son, L. M., 702
Ionescu, C. N., 767
Ionescu, Th., 1151
Ionizing Corp. of America, 267, 268
Iotsitch, 565
Ipatieff, V. N., 92, 93, 96, 155, 199, 200, 202, 205, 207, 208, 306, 314, 431, 591-596, 598, 599, 602, 605, 634, 635, 637, 639, 640, 642, 646, 654, 662-665, 669, 699, 871, 919, 1017, 1301, 1302
Ireton, H. J. C., 267
Isacescu, D. A., 205, 1099, 1102
Isagulyantz, V. I., 565, 823, 824
Isenbeck, B., 1115
Isham, R. M., 169, 393, 517, 593
Ishida, M., 1206
Ishii, N., 1036
Ishikawa, H., 54, 167, 180
Iskra, E. V., 517
Isom, E. C., 261
Israel, R. G., 160
Iterson, J. R. van, 1156
Ittner, M. H., 976
Ivannikov, P. Y., 337, 338, 339, 878
Ivanov, A. A., 696
Ivanov, I. I., 143, 589, 668
Ivanov, I. Z., 32, 646, 963
Ivanov, K. I., 843, 854, 941, 964, 1015
Ivanova, E. G., 1156
Ivanova, K. A., 173
Ivanova, M., 674
Ivanovszky, L., 15, 1176
Ivaschenko, Ya. N., 490
Ivy, A. C., 1262
Izard, H. E., 540, 544
Izmailov, G. K., 1105

J

Jachzel, J., 1220
Jackson, D. E., 711, 1259
Jackson, E. L., 627
Jackson, E. W., 1061
Jackson, J. S., 1184
Jackson, K. S., 781
Jacobi, C., 794
Jacobs, C. J., 1279, 1280, 1283, 1285
Jacobsohn, F., 1205
Jacobson, D. L., 465
Jacobson, P., 485
Jacobson, R. A., 705, 706, 708
Jacobus, G., 1240
Jacque, L., 269
Jaeger, A. O., 335, 789, 915, 945, 946, 949, 950, 952, 954, 958, 959, 960
Jaffe, E., 570, 572
Jage, F., 957
Jahrstorfer, M., 353, 1057
Jakes, M., 1192
Jakob, L., 651
Jakobowicz, W., 1184
Jakosky, J. J., 226, 244, 255
Jakuba, E., 1125
James, J. H., 843, 850, 862, 863, 869, 881, 966, 967, 1047, 1053, 1056, 1060
Jamison, E. A., 26
Jannek, J., 197, 813
Janney, W. M., 1162
Janot, M., 1151
Janssen, C., 939, 940
Janssen, H. J., 1061
Janssen, P., 396, 398
Jansson, J. I., 413
Jarmans, R., 1266
Jatkar, S. K. K., 379
Jeannin, R., 932
Jeason, C. A., III, 1086
Jeliner, H., 859, 946, 965
Jenemann, J. A., 380

Jenkins, R. L., 783
Jenkins, S. S., 452
Jenkins, V. N., 197
Jenkins Petroleum Process Co., 130
Jensen, K. A., 479
Jentzsch, H., 1000
Jessel, R., 1325
Jessen, F. W., 24
Jeunehomme, W., 780
Jezierski, T. W., 469
Jirouch, E. A., 580
Johannsen, A., 946, 950, 951
Johler, W. W., 413, 800
Johnson, E. W., 710
Johnson, T. B., 527
Johnson, T. W., 905
Johnston, C. G., 528
Johnston, F., 310
Johnston, H. L., 22
Johnston, J. E. A., 1266
Johnston, R. L., 1262
Johnston, W. R., 50, 51
Johnstone, G. A., 1257
Johnstone, W., 400
Jones, C. L., 539, 578
Jones, D. G., 48, 232
Jones, D. T., 1097
Jones, F. A., 439
Jones, G. W., 732, 980, 983, 984, 985, 989, 996
Jones, H. J., 1169
Jones, H. L., 737, 946
Jones, L. D., 495, 745, 753
Jones, M., 681
Jones, W. J., 686
Jong, H. W. de, 444
Jordan, H., 606
Jordan, H. H., 577
Jordan, J., 1007
Jorissen, W. P., 922
Joseph, A., 126, 127, 128
Joshua, W. P., 164, 175, 284, 285, 292, 294, 322, 340
Jost, W., 769, 1005
Jostes, F., 1110
Juge-Boirard, M. G., 354
Juliard, A., 267
Jung, R., 168, 169
Jungers, J. C., 266, 725
Justi, E., 14, 461, 1339

K

Kacer, F., 957
Kadmer, E., 1149
Kadmer, E. H., 1214
Kägi, H., 809
Kaftanov, S. V., 135
Kafuku, K., 179
Kagan, M. Ya., 333, 421, 422, 714, 889
Kaganova, E. M., 290
Kahn, E. J., 887
Kahn, M. H., 1263
Kaiser, W. J., 1120
Kaisler, P., 665
Kajimoto, S., 1033
Kaladzhal, R., 577
Kalb, L., 559
Kalichevsky, V. A., 28, 37, 477, 668, 942, 1163, 1173, 1190, 1192, 1208, 1214
Kalischer, G., 1086
Kallam, F. L., 24
Kambli, W., 532
Kamioka, T., 1096
Kamm, O., 583
Kamusher, H., 73
Kane, G. P., 22
Kane, H. F., 1257
Kane, T., 301, 307, 308
Kaneko, G. K., 902
Kanep, E. K., 108, 109, 136, 137, 173, 177
Kanga, D. D., 467, 720
Kanhofer, E. R., 1016
Kantorowicz, H., 1192
Kao, C. H., 828
Kapelyushnikov, M., 140
Kaplan, W., 123, 141, 144
Kaplin, P., 674
Karasik, M. M., 109
Karavaev, N. M., 135, 144, 145, 909
Karishin, A., 955
Karlash, P. V., 784
Karr, C. J., 711
Karrer, P., 621
Karskii, N. N., 909
Karzhavin, V. A., 225, 234, 269, 270, 271, 272, 870, 1128
Karzhev, V. I., 93, 135, 145, 186
Kaselitz, O., 503
Kashtanov, L. I., 53, 218, 992
Kasper, C., 32
Kass, C. B., 1027
Kassel, L. S., 15, 52, 53, 55, 68, 165, 1280, 1283, 1291
Kassler, R., 516
Kas'yanova, N., 1113
Kato, O., 717
Kato, T., 136
Kato, Y., 703
Kattek, F., 497
Katti, M. C. T., 424
Katz, J., 947
Katz, M., 92
Katzman, S. V., 108, 109, 138, 144, 172, 310
Katznel'son, I. L., 953
Katznelson, M. M., 447
Kaufman, G., 1107, 1114
Kaufmann, C., 242, 251
Kaufmann, H. L., 261
Kaufmann, H. P., 711, 1153
Kautter, C. T., 516, 567
Kawamichi, K., 1236
Kay, W. B., 1312, 1318, 1322, 1323
Kazanskii, B. A., 16, 34, 90, 91, 92, 144, 171, 172, 173, 508, 510, 631
Kazarian, L., 721
Kazarnovskaya, M. A., 454
Kazarnovskii, S. N., 461, 713, 718
Kazarnovskii, Ya. S., 992
Kedrinskii, V. V., 532, 537, 567
Keene, W. L., 223
Kegel, A. H., 727
Keiser, B., 577, 1075, 1086
Keiser, E. H., 702, 711
Keith, J. R., 37
Keith, P. C., Jr., 41, 97, 99, 102, 106, 107, 109, 116, 118, 119, 120, 631, 654, 658, 1201
Kekulé, A., 622
Kelbovskaya, M. K., 903
Kell, K., 1199, 1202
Keller, K., 758, 810, 828, 1083
Keller, T. P., 224, 241
Kellerman, M. E., 1115
Kelley, K. K., 369, 1279, 1285, 1293
Kellogg, C. M., 434, 530
Kellogg Co., 710
Kelly, C. I., 932, 1173
Kemmer, H., 1241
Kemp, J. D., 1280
Kemula, W., 266, 703
Kendall, A. R., 547
Kendall, H. S., 159
Kendall, M. T., 44
Kenigsberg, Z., 997
Kennedy, C. C., 342, 407
Kennedy, H. S., 22
Kennedy, R. E., 732, 980, 983, 984, 985, 989
Kennedy, T., 1076
Kenner, J., 96, 447
Keppeler, G., 29
Kern, J. G., 575, 578
Kester, E. B., 1101
Kettenring, L. C., 731
Kettle, R. L., 841
Keunecke, E., 964
Kewley, J., 11, 1184
Keyes, D. B., 343, 462
Keyssner, E., 715, 719
Keyte, W. R., 19
Khachadurova, E. M., 334
Khaiman, S., 111, 758, 817
Khain, S. S., 376, 1080
Khakhaeva, V., 733
Khakham, I. B., 461
Khambata, B. S., 652
Kharasch, M. S., 315, 316, 317, 318, 628, 686, 716, 723
Kharmandar'yan, M. O., 458
Kharzhavina, N. A., 1240
Kheifetz, A., 1069
Khisin, Ya. I., 831, 1069
Khokhlovkin, M. A., 650, 692
Kholler, V. A., 145
Khomutin, M. S., 494, 709
Khrenova, M., 461
Khrenova, Z. A., 165
Khutoretzkaya, S. N. 173
Kibirklitis, S. G., 173
Kiemstedt, H., 905, 906
Kiersted, W., 433
Killeffer, D. H., 194, 732, 745
Killian, D. B., 706, 722, 723, 724
Kimball, G. E., 683
Kine, J., 732
Kinetic Chemicals, Inc., 733, 735, 736, 737, 747, 748, 811
King, A. M., 1113
King, E. C., 1078
King, H., 335
King, J. C., 1128
King, R. J., 1078
King, R. O., 935, 996, 1019, 1055
King, Robert J., Co., Inc., 1078
King, W. A., 11, 834
King, W. H., 876, 881, 966
Kingo, T., 241
Kinney, A. M., 1078
Kinumaki, S., 502
Kiprianov, A. I., 726, 767, 955
Kirby, J. E. ,681, 682, 706
Kirchhof, F., 674
Kirchhoff, G., 720
Kireev, V. A., 334, 535, 554, 701
Kirk, R. C., 954
Kirn, E. R., 370
Kirner, W. R., 526
Kirrmann, A., 379, 382, 401
Kirsanov, A. V., 490, 1044
Kirschbaum, L., 1193
Kirschbraun, L., 1214, 1219, 1220, 1221
Kirstahler, A., 479, 480, 487, 1120
Kishline, F. F., 1034
Kishner, N., 762, 807
Kissel, H., 1093, 1096
Kisselev, V. S., 1115
Kissling, R., 1161
Kistiakowsky, G. B., 82, 90, 410, 437, 652, 806, 807, 902, 1277, 1283, 1284
Kistler, S. S., 446
Kistyakovskii, V., 1325
Kitaitzev, V. A., 467
Kitamura, R., 471
Kitchin, D. W., 251

K. K. Umeda Kimô Senshoku Kôjô, 747
Klaas, R., 354
Klabina, T. I., 102, 103
Klarmann, E., 604
Klason, P., 481
Klass, I. A., 1007
Klatt, R., 30, 31, 89, 251, 859, 946, 965, 1151, 1152
Klazinga, W. M., 204, 643
Klebanskii, A. L., 507, 532, 546, 609, 681, 687, 706, 707, 708, 797
Klebstattel, C. A., 1115
Kleiber, C. E., 1044
Klein, D. X., 472
Klein, H., 353, 753, 1218
Klein, O., 710
Klein, W., 192
Kleindorfer, G. E., 1258
Kleiner, M. J., 570
Kleinert, H., 1213, 1220, 1221
Kleinschmidt, R. V., 260, 284, 1271, 1272, 1295, 1302
Klemenc, A., 725
Klempt, W., 274, 277
Klever, F. W., 794
Klevke, E. A., 1128
Klimmer, O., 580
Klimov, B. K., 1240
Kline, G. M., 400, 633, 755
Kling, K., 22
Klingmann, G. H., 1220
Klingstedt, F. W., 621
Klinkenberg, A., 15
Klipstein, E. C., & Sons Co., 563
Klipstein, K. H., 563
Klit, A., 206
Klokkers, P. J., 1167
Kluykvin, I., 1194
Klyukvin, N. A., 54, 1229
Klyukvina, S. S., 54
Knapp, A., 7
Knauss, C. A., 1115
Knibbs, N. V. S., 953
Knick, H., 1139
Knight, H., 1112, 1115
Knight, O. S., 567
Knoche, E., 669, 1154
Knoop, H., 537
Knorr, L., 561, 583
Knowles, A. S., 230
Knowles, E. C., 453, 1187, 1202
Knunyantz, I. L., 561, 565
Kobayashi, K., 54, 167, 180
Kobayashi, R., 40, 755, 756, 758, 807, 817, 937, 1033
Kobe, K. A., 869, 1061, 1062, 1063, 1123, 1129
Kobelev, V. A., 786
Koblyanskii, G. G., 173, 347, 650, 651
Kobozev, N. I., 53, 54, 218, 257, 992
Kobrin, S. M., 53, 218
Kobuil'skaya, M. V., 70, 199
Koch, H., 214, 671, 813, 814, 815, 1224, 1225, 1227, 1229, 1241, 1242, 1245, 1249, 1250, 1251, 1253, 1254, 1255
Koch, T., 578
Koch, W., 543
Kochneva, M. P., 916
Kodak-Pathé, 507, 541
Kodama, S., 1229
Köbel, H., 1244, 1248
Köberle, K., 790
Köhler, H., 327, 480
Koeneman, J. K., 26
Koenigs, W., 606
Kõrding, P., 569
Kõrting, A., 1039
Koetschau, R., 1132, 1163
Kofman, L. S., 173, 177
Kogan, A. M., 173
Kogan, E., 975
Kogan, G. M., 677
Kogerman, P. N., 911
Kohler, E. P., 473
Kohlhardt, K., 135
Kohlrausch, K. W. F., 1183
Kok, A. J. de, 311, 643
Kok, W. J. C. de, 1145, 1153
Kollek, L., 510
Koller, K., 458
Kollmann, T., 525
Kolodkina, L., 463
Kolpenskaya, T. P., 178
Kolthoff, I. M., 424
Komarewsky, V. I., 92, 93, 96, 200, 205, 207, 400, 594, 599, 602, 665, 1302
Komarov, V. A., 674
Komissarov, J. F., 525
Komppa, G., 902
Kondakov, I. L., 370
Koninklijke Vereen Tapijtfabrieken, 1084
Kon'kova, V. A., 753
Konowalow, M. I., 1090, 1094
Konrad, E., 172
Kontol Co., 1075
Kontorova, T. A., 1001
Koo, E. C., 136, 1035
Koolman, C. ten D., 464
Koopmans, H., 1038
Kootz, H., 647
Kopelevich, G. V., 484, 1161
Kopeliovich, E. L., 458
Koppelmann, A., 214
Koppers Co. of Delaware, 169, 458, 459, 465, 468
Koppers, Heinrich, G. m. b. H., 458
Koppers', Heinrich, Industrieele Maatschappij N. V., 458
Korneich, K. F., 767
Korotkov, A. A., 699
Korshak, V., 877
Koryushenko, Z., 674
Korzhev, P. P., 884, 885
Kosolapov, Z. E., 331, 831
Kossendey, F., 1155
Koton, M. M., 338, 1022
Kotrelev, A. N., 1162
Kovalik, M. S., 170
Kowalewski, S., 342, 638, 878
Koyano, T., 260
Kozeshkov, K. A., 770
Kozlov, N. S., 334, 705, 719
Kozlovskaya, A. V., 173
Kozuireva, E. I., 33, 1154
Kraemer, G., 591, 1206
Kraemer, M. H., 27
Kränzlein, G., 772, 794
Krainii, P. Y., 331
Krall, H. G., 774
Kramer, G. A., 325, 393, 458, 642
Krantz, J. C., 711
Krapp, K., 255
Krasavin, S. F., 793
Krase, N. W., 1246
Krasheninnikova, V. M., 420
Krasil'shchikov, A. I., 1323
Krasnokutski, G. I., 95
Krassilchik, A., 629, 1152
Krassukii, K., 547, 585
Krauch, C., 1188
Kraus, R., 466
Krause, A. H., 945, 960
Krause, E., 767
Krauskopf, K. B., 887
Krauss, A., 701
Krauss, H., 561
Krauz, C., 1090
Krauze, K. E., 247
Krauze, M. V., 636, 639, 641
Krauze, V. P., 173, 389
Kravetz, V.E., 674
Krebs Pigment and Color Corp., 248, 1117
Krechkov, N. P., 705
Krefft, O. T., 759
Kreidl, I., 950, 964
Kreighbaum, H. S., 542
Krein, S. E., 855, 874, 932, 936, 937
Kreiselman, J., 1257
Kreitzer, G. D., 1214
Krekeler, H., 41, 1163
Krendel, A. S., 467
Kreshkov, A. P., 843, 971, 978
Krestinskii, V. N., 903
Kreulen, D. J. W., 1181
Kreutzer, A., 1107
Krey, W., 557, 805
Kriewitz, O., 624
Krijgsman, C., 939, 940
Krishman, P. S., 371
Krishnaswami, K. R., 22
Kritchevsky, W., 373, 549
Krivonos, F. F., 779
Kroeger, J. W., 724
Kropfhammer, G., 543
Krovatzkii, 870
Kruber, O., 998
Kruglaya, N. B., 969
Krupuishev, M. A., 173
Krzikalla, H., 679
Kubo, K., 1175
Kubo, M., 367
Kubul'nek, A. Ya., 131, 165
Kucera, J. J., 581
Kuchinskaya, K. I., 520
Kuczyński, H., 431
Kuczyński, T., 43
Kudinov, A. V., 178
Kudo, K., 119
Kudryavtzev, N. A., 87, 645
Kueck, P. D., 257
Kuhn, J., 136, 154, 196, 219, 227, 272, 871
Kuentzel, W. E., 151, 214, 631, 637, 640, 672
Kuster, H., 1228, 1232, 1233, 1236, 1241, 1242
Küster, F. K., 483
Küster, F. W., 1155
Kuhl, P. E., 459
Kuhring, M. S., 1035
Kuhrmann, F., 209, 918
Kuibina, L. I., 650
Kunc, J., 814
Kungl. Arméförvaltningens Artillerideparternent, 189
Kunz, E. C., 496
Kunz, M. A., 790
Kunze, G., 968
Kunznetzova, A. N., 972
Kurlin, M. V., 940
Kurlina, A. M., 940
Kurokawa, M., 1006
Kurtz, S. S., Jr., 486, 1171, 1173, 1178
Kuruindin, K. S., 144, 668, 909, 916
Kushelevskii, B., 123
Kusner, T. S., 726
Kuss, E., 1018
Kutzenok, L., 495
Kuwata, T., 717, 906
Kuzin, S. A., 975
Kvalnes, H. M., 50
Kwal, B., 928
Kyrides, L. P., 330, 525, 577, 794, 816
Kyropoulos, S., 37

L

Labarthe, J. Jr., 1057
Lacey, R., 44

Lacey, W. N., 9, 14, 15, 16, 1307, 1334, 1335, 1337, 1339, 1340
Lachman, A., 668, 928, 929
Lackey, R. W., 836
Lacombe, A. E., 470
Lacy, B. S., 736
Lacy, K. B., 309, 359
Ladd, E. C., 749
Ladenburg, A., 527, 623
Ladigina, L. V., 768
Laffitte, P., 980
Lahee, F. H., 19
Lahocinski, Z., 1202
Lai, T. Y., 722
Laird, F. N., 1169
Laird, R. F., 733
Lalande, A., 329
Lambert, P., 353
Lampe, B., 1185
Lamson, P. D., 1256
Landa, Mme., 35
Landa, S., 32, 34, 35
Landgraf, A., 466, 1125
Landsberg, G., 1181
Landsteiner, K., 1094
Lane, E. C., 12
Lang, A., 929
Lang, F., 1154
Lang, H. R., 1325
Lang, J. W., 58, 59, 149, 1139, 1143
Langdon, H. H., 1149
Lange, H., 587
Lange, W., 767
Langedijk, S. L., 291, 397, 518, 627, 1081
Langheinrich, H., 186
Langkammerer, C. M., 819
Langseth, A., 206
Langwell, H., 383, 403, 416
Langworthy, M. L., 433
Lanin, V. A., 1240
Lankelma, H. P., 916, 918
Lansing, A. C., 354
Lapeyrouse, M., 1176
Lapkin, I. I., 23, 29
Lapp, H., 1261
Larchar, A. W., 547
Lardon, A., 887
Larin, A. Y., 675
Larionov, Z., 335
Larson, A. T., 279, 288, 432, 446, 626, 830, 893, 894, 957
Larson, C. M., 1176
La soc. anon. des ateliers de constructions mécaniques Escher Wyss, 504
Lassiat, R. C., 126
Latimer, W. M., 1279, 1285
Latzko, W., 1220
Lauer, C. E., 1107
Lauer, F., 273
Lauer, W. M., 318, 565, 692, 819
Laughlin, K. C., 15, 411, 645
Lauter, W. M., 497
Lavrov, F. A., 998, 1001
Lavrovskii, K. P., 1145
Law, G. H., 435, 441, 442, 586
Lawrence, A. S. C., 632
Lawrence, F. I. L., 50, 186, 191
Lawrence, R. E., 1041
Lawrie, L. G., 559
Lawson, W. E., 826
Lazar, A., 42, 1064
Lazar, O., 171
Lazarev, N. V., 1262
Lazell, C. L., 527
Lazier, W. A., 307, 351, 420, 432, 1120
Leah, A. S., 1007
Leahy, M. J., 459, 1018
Leake, C. D., 1260, 1261
Leaper, P. J., 429
Leatherman, M., 1086
LeBaron, R. F., 389, 392, 393
LeBas, J., 733
Lebeau, P., 722, 1124
Lebedev, S. V., 87, 88, 173, 347, 389, 642, 643, 645, 650, 651, 674, 676, 824
Lebedeva, N. I., 556
Lebo, R. B., 305, 357, 365, 367, 407
LeBoulenger, P., 401
Le Chatelier, H., 1270
Leckie, A. H., 441
Le Clerc, G., 1229, 1231
Leclerq, J., 710
Lederer, E. L., 103, 130, 855, 931, 1084, 1118, 1169, 1170
Leder-Packendorff, L., 445, 1099
Lee, A. R., 1174, 1206, 1207, 1213
Lee, I. E., 915, 917
Lee, P. J. van der, 743
Lee, W. M., 309, 312, 463, 472, 604
Leendertse, J. J., 138, 179, 203, 204, 210, 216, 310, 311, 643, 645, 1177
Leermakers, J. A., 1022
Lefebvre, H., 1229, 1231
Le Fevre, C. G., 441
Le Fevre, R. J. W., 441
Le Fevre, W. J., 827
Leffman, H., 1171
Le Fly Tox, 538
Lefort, T. E., 552, 893
Legatski, T. W., 25
Légé, E. G. M. R., 1043
Lehman, K. B., 727, 743
Lehmann, E., 527, 690
Lehmann, I. I., 1261
Lehn and Fink, Inc., 604
Lehnherr, E. R., 733
Leibush, A. G., 271, 870, 1128
Leighton, P. A., 267, 1022
Lel'chuk, S. L., 338, 339
Lelgemann, W., 112, 198, 1102
Lemcke, W., 252
Lenher, S., 639, 893, 902, 903
Leopold, R., 427
Lepigre, A. L., 566
Lepkovsky, S., 549
Leprince-Ringuet, F., 984
Lerer, M., 827, 1172
LeRoi, E. J., 105
Lesbre, M., 829
Leslie, E. H., 1034
Leslie, R. T., 30-34, 42, 942, 1179
Lespieau, R., 1183
"Les savons nouveaux" compagnie Sapoflor, 575
Lessing, R., 1305
Letort, M., 884
Leupold, E., 8
Levaillant, R., 525
Levene, H. H. L., 810
Lever Bros., Ltd., 1112
Levi, G. R., 481, 482
Levin, H., 917, 1165, 1218
Levina, R. Y., 93, 94, 143, 764
Levine, A. A., 710, 727, 742
Levine, I., 434, 471, 625
Levine, V. E., 1151
Levinson, B. L., 95, 99, 645
Levkopulo, N., 964
Levy, È., 570
Levy, L. A., 704
Lewers, W. W., 1079
Lewis, A. W., 935
Lewis, B., 1005
Lewis, D., 1257
Lewis, D. C., 567
Lewis, G. C., 240
Lewis, G. N., 344, 725, 1270-1272, 1274, 1277, 1285, 1293, 1296-1298, 1306
Lewis, H. A., 533
Lewis, W. B., 1258
Lewis, W. K., 103, 333, 869, 917, 1173, 1319-1323, 1325, 1335, 1340
Lewis, W. R., 425
Lewis Differential Co., 539
Leznov, N. S., 949
Libermann, D., 413
Liberthson, L., 530, 1073, 1074, 1219
Lichty, L. C., 1035
Liddel, U., 32
Lidow, J. P., 1117
Lieber, E., 355, 371
Lieberman, A., 257
Liebmann, A., 401
Liefde, W. C. de, 701
Lienhart, J., 1177
Lievre, G. P., 1075
Light, D. W., 1279
Lightfoot, J. H., 24
Ligtenberg, H. I., 216
Likhosherstov, M. V., 173, 347, 509, 510, 516, 520, 627, 753, 779
Likhusin, K. P., 964, 1064, 1069
Lilly, R. M., 1160
Limburg, H., 1072, 1074, 1116, 1217
Linchk, E., 171, 189
Lincoln, B. H., 758
Lind, S. C., 257, 264, 267, 703, 725
Linde, N.v.d., 463
Lindeke, H. F., 44
Lindenbaum, E., 844
Lindenberg, A., 424
Linder, E. G., 257, 260
Linder, K., 1076
Lindner, D., 746
Lindsay, J. D., 1333
Linn, C. B., 58, 63, 66
Linnett, J. W., 479
Linstead, R. P., 318
Linton, E. C., 580
Lipp, A., 623
Lipp, J. W., 891
Lippmann, E., 630
Lisman, J. H. C., 1337
Lister, F. V., 1220
Litinsky, L., 975
Little, A. D., 46
Little, A. D., Inc., 46, 260, 627
Littlefield, J. B., 466, 733
Liu, C., 301
Liu, Y. P., 296, 410
Livanova, O., 302
Livingston, R., 264, 266, 703
Livraghi, E., 1039
Livshitz, I. A., 174, 347, 645
Livshitz, S. E., 70, 199, 757
Lloyd, L. L., 377
Lloyd-Evans, B. J., 1007
Lobeck, H., 273
Lobley, A. G., 1044
Loch, S., 190
Locher, J., 1094, 1096
Lockspeiser, B., 538
Loder, D. J., 614
Loebel, A., 672
Loevenich, J., 773
Lowy, J., 733
Logan, W. B., 636, 666, 1105
Loges, A. C., 732
Logvinova, N. I., 745
Lohmann, H., 562
Lohrengel, W., 743, 1035, 1037
Lolkema, J., 31
Lomakin, G. A., 540
Lomanovich, A., 1112

Lommen, F. W., 808
Lone Star Gas Co., 461
Longley, W. R., 1271
Longobardi, E., 46
Looker, C. D., 1101
Loomis, N. E., 1097
Lorang, H. F. J., 397, 420
Lorne, H. T., 1188
Lott, W. A., 336, 528
Louis, M., 1037
Lovell, W. G., 201, 1012, 1019, 1024, 1030, 1098
Lowry, C. D., Jr., 669, 703, 908, 913, 914, 916-920, 922-926
Lowy, A., 640
Lozovoi, A. V., 135
Lozovskii, M., 332
Lubatti, O. F., 556, 557, 566
Lubri-Zol Corp., 790
Lubri-Zol Development Corp., 758
Lucas, G. H. W., 1265
Lucas, H. J., 294, 296, 410, 547, 588, 897, 1146, 1303
Lucas, O. D., 194
Luchsinger, W., 737
Lucke, B., 528
Luckhardt, A. B., 1256-1258
Ludeman, C. G., 917
Ludwig, E. H. B., 26
Lübke, A., 728
Lühder, E., 328, 329
Lühl, H. A., 789
Luke, C. D., 1322, 1323
Lundquist, J. T., 418, 818
Lundy, J. S., 1257
Lunt, G. P., 380
Lur'e, M. A., 651, 673
Luther, M., 865, 964, 971, 973, 975, 976
Luther, R., 778
Lutz, R., 697
Lyons, F. H., 790
Lyubarskii, G. D., 421, 714, 889
Lyubimov, A. L., 1109

M

Maass, O., 15, 304, 306, 722
McAdams, W. H., 1173, 1335, 1340
McAfee, A. M., 197
McAleer Mfg. Co., 532
McAlevy, A., 1152
McAllister, S. H., 450, 548
Macallum, A. D., 281, 428
McBain, J. W., 330, 755, 1113
McBee, E. T., 740, 750, 752, 754, 766
McCarty, B. Y., 43, 433, 434, 453, 495, 507, 513, 543, 546, 745, 789
McCluer, W. B., 1172-1174, 1176
McCollum, R., 1192
McConnaughay, K. E., 1215
McConnell, E. B., 918, 1205
McConnell, T. A., 1175
McCormick, H. P., 457
McCormick & Co., 732
MacCoull, N., 1029
McCoy, A. W., 19
McCracken, R., 771
McCulloch, A., 227
MacCulloch, A. F., 336, 381
McDaniel, E. I., 507
MacDonald, G. D., 1127
MacDonald, J. McL., 901
McDonald, R., 1258
McDonald, R. D., 851, 896, 902
MacDonald, R. T., 725
McDuffie, W. C., 1205
McEllroy, W. S., 1259
McElroy, K. P., 519
McElvain, S. M., 772, 773
MacGillivray, W. E., 1138
McGrew, R. V., 901, 1174
Macháček, V., 32, 34, 35
Macht, F., 1213
McHutton, L. P., 925
McIlhiney, P. C., 1153
McIlvain, J. M., 1164
McIntyre, G., 538, 930, 1080
Mack, C., 1186, 1198, 1206, 1211
Mack, E., Jr., 554, 555
McKay, W. B., 569
McKee, R. H., 831, 953, 1091
MacKenzie, K. G., 1056, 1193
McKesson, C. L., 1221
McKittrick, D. S., 530
MacLang, J., 745
MacLaren, F. H., 758, 817, 1075
MacLean, G., 476
McLennan, J. C., 267
McMahon, F. A., 720
McMillan, W. A., 30, 701, 1138, 1140, 1145
McMullan, E. W., 917
McNab, J. G., 723
McNab, M. C., 315, 317, 716, 723
McNally, W. D., 727
McNamara, L., 909
McNary, R. R., 733, 734, 736
McNeil, C. P., 1204, 1205
Macouski, E., 184
McQuaid, H. S., 576
McQuillen, A., 725
MacRill, J. R., 577
McShan, W. H., 413, 800
Macura, K., 1068
Maddocks, C. B., 416
Madsen, E. H., 729
Madsen, L. M., 1214
Magnesium Development Corp., 731
Magness, L. F., 1038
Mahood, S. A., 88
Maier, C. G., 1048, 1049
Mailhe, A., 88, 645, 775
Maillard, A., 935, 940
Mainz, H., 928
Maiofis, L. S., 730, 733
Mair, B. J., 31, 36, 37, 40, 433, 1155, 1172
Maison Camus Duchemin (Soc. anon.), 446
Maizels, M., 1261
Major, R. T., 528, 529
Makashina, A. N., 651
Makishima, G., 533
Makkink, J. P., 204, 210, 643
Makray, I., 1151
Maksimovich, G., 1114
Makushinskaya, N. S., 1166
Mal, R. S., 367
Maleeva, E., 876
Malinkina, A. S., 174
Malinovskii, A. E., 986, 1001, 1007
Malishev, B. W., 483, 594, 637, 665, 669
Malisoff, W. M., 470, 471, 478, 488, 489, 604, 1158, 1163
Maliyantz, A. A., 490
Mallinckrodt Chemical Works, 895
Mallory, P. R., & Co., Inc., 539
Malm, C. J., 380, 496, 588
Maltha, P., 549
Mal'tzeva, A. L., 651
Malzac, A. C., 733, 738
Maman, 15
Mamedaliev, Yu. G., 493
Mamisao, J. P., 1039
Manchot, W., 702
Mancini, M. A., 537
Mandelbaum, M. R., 666, 667, 928
Mandelstam, L., 1181
Mandlekar, M. R., 992
Mangelsdorf, T. A., 38
Manheimer, J., 1204
Manikov, A., 335
Manley, R. E., 43, 45, 433, 488, 636, 666, 667
Mann, C. A., 486
Mann, M. D., Jr., 357
Manokhina, O., 543
Manughevici, C., 155, 196
Marburg, E. C., 465
Marchant, G., 540
Marck, L. F., 293
Marconi, M. A., 112
Marcusson, J., 977, 1186, 1188, 1190, 1191, 1193, 1194
Marder, M., 1030, 1031, 1177, 1181, 1243
Mardles, E. W. J., 911, 914, 915, 933, 938, 1116
Marek, L. F., 58, 61, 66, 133
Mares, J. R., 732, 778
Margolis, E. I., 92
Margolis, E. T., 686
Margolis, L., 495
Margules, E., 709, 753, 801
Margulis, G. A., 271
Maricq, L., 354
Mark, H., 632
Marko, D. M., 29
Markosova, M. I., 34
Markovich, M. B., 140, 161, 174, 357, 387, 393, 1142
Markownikow, W. B., 34, 298, 876, 1095
Markwick, A. H. D., 1207
Marriott, J. A., 531, 1092
Marsene Corp. of America, 686
Marshall, A. L., 1277
Marshall, C. A., 1030
Marti, W. C., 744
Martin, E. L., 851
Martin, F., 214
Martin, H., 902, 1077, 1149
Martin, L. F., 595
Martin, R., 452
Martin, S. M., Jr., 930
Martinek, M. J., 744
Marvel, C. S., 616-618, 724, 1082
Marvin, C. F., Jr., 1006
Marvin, S. W., 528
Marx, K., 558, 789, 825, 1078
Marx, W., 334
Mascarello, G., 852
Maschmeijer, A., Jr., Inc., 416
Maschmeijer, A. J. H., 416
Mashbitz, L. M., 424
Masina, M. P., 1150
Maslov, P. S., 33, 1154
Mason, C. W., 39, 755
Mason, I. D., 496
Mason, J. W., 574
Massart, L., 16
Masumyan, V., 1104
Mate, B., 551
Maters, C., 900
Mathes, W., 782, 786
Matheson, G. L., 486
Mathias, H., 1080
Mathieson Alkali Works, 447, 1057
Mathur, R. N., 367
Matignon, C., 71, 154, 273, 557, 642
Matsushita, Y., 39
Matthews, E. D., 327
Mattier, M., 828
Mattison, E. L., 735, 736, 808
Mattox, W. J., 163, 699, 1132, 1135, 1142
Matuszak, M. P., 1140

Matzkevich, R. M., 560
Mauersberger, E. A., 1061
Maurel, A., 756, 759
Mauthe, G., 562
Maverick, G. M., 758
May, R., 1076
Maybery, C. F., 834
Mayer, J. E., 1280
Mayer, K. E., 317
Mayer, M. G., 1280
Mayer, N., 24, 913, 1199
Mayo, F. R., 315, 686, 716
Mayor, Y., 713, 1105
Mazonski, T., 312
Mead, B., 917, 1114
Mead, F. C., Jr., 95
Meadow, J. R., 471, 485
Meanes, E. A., 1172
Mears, W. H., 652
Mechling, G. S., 1266
Medard, L., 1092
Medvedev, S., 381, 674, 727, 728, 796, 900
Meek, W. J., 1267
Meerwein, H., 422, 540
Meharg, V. E., 878
Meidert, F., 1115
Meigs, J. V., 130, 1034
Meigs, Bassett & Slaughter, 468
Meinel, K., 531
Meiner, H., 1155
Meinert, R. E., 88
Meinhard, P., 1151
Meissner, M., 554
Meister, R., 887
Mekler, L. A., 133
Meldola, R., 320
Mellon, M. G., 370, 375
Mel'nikov, N. N., 432, 479
Melsen, J. A. van, 390, 443
Meltsner, M., 570
Melville, H. W., 265
Mendenhall, W. R., 16
Menke, J. B., 791
Menschutkin, N., 1118
Merck & Co., 328, 330, 528, 529
Merck, F., 529
Merck, K., 529
Merck, L., 529
Merck, W., 529
Merley, S. R., 315, 359, 365, 377, 396, 397, 408, 1081
Merrell, W. S., Co., 480
Merrill, D. R., 43, 530, 545, 575, 667, 1107
Merrimac Chemical Co., 305, 327, 364
Merz, V., 747
Merzlikin, F., 674
Meschorer, J., 465
Meshcheriakov, A. P., 72, 87, 202, 643
Meshel, F., 1194
Messinger, J., 424
Metallges. A.-G., 457, 464
Metcalf, N. W., 783
Metzger, F. J., 169, 282, 283, 291
Metzger, H., 1176
Meulengracht, E., 1261
Meunier, L., 1221
Meunier, P. L., 401
Meusel, A., 1242
Meuser, L., 429
Meuwsen, A., 345
Meyer, E., 558
Meyer, E. G. E., 1039
Meyer, G., 1128
Meyer, H., 382, 401
Meyer, I., 580
Meyer, K., 1229, 1231, 1240, 1248, 1249
Meyer, K. H., 15
Meyer, R., 720
Meyer, V., 720, 1087, 1094, 1096
Meyers, C. H., 824
Meyers, D. N., 1217
Meyersheim, G., 1192
Mezhebovskaya, E., 323, 386, 388, 917, 923
Michael, A., 321, 520, 622, 1082
Michel, R., 595
Michigan State Board of Agriculture, 416
Michnovska, L., 1142
Michot-Dupont, G. F., 136, 268
Mid-Continent Petroleum Corp., 163, 530
Midgley, T., Jr., 733, 734, 736-738, 748
Midland Steel Products Co., 1114
Mid-West Chemical Co., 1077
Mignonac, G., 89, 258, 703
Migray, E., 1168
Mikeska, L. A., 36, 38
Mikhailov, B. M., 87, 92, 93, 172, 421, 714
Mikhailova, M. N., 922
Mikhel'son, E. M., 458
Mikhlin, N. E., 195
Milas, N. A., 547, 895, 922, 1152
Milchalske, A., 574
Millar, R. W., 283, 293, 712
Miller, C. C., 163, 1175
Miller, E. B., 669
Miller, F. L., 674
Miller, G. H., 1262
Miller, H., 1037
Miller, H. F., 824
Miller, J. C., 22
Miller, L. P., 519
Miller, M. B., 43
Miller, M. B., & Co., 43
Miller, R. W., 158
Miller, S. E., 692
Miller, W. E., 980, 989
Milliken, M. G., 538
Mills, L. E., 507, 732, 746, 781, 790, 916
Miloslavskii, S. Ya., 254
Milovidova, N. V., 1153
Mil'shin, 929
Miltschitzsky, G., 737
Minchin, S. T., 1184
Mineral Akt.-Ges. Brig., 1216, 1219
Minimax A.-G., 505
Minsk, L. M., 496
Minter, C. C., 1011, 1150
Mirzakulieva, M. I., 1069
Mirzoeva, E., 1075
Miscall, J., 1217
Mischonsniky, S., 1132
Missbach, E. C., 730, 731
Mitchell, J. G., 1206
Mitchell, M. B., 1039
Mitchell, S., 1101
Mitchell, W., 715
Mithoff, R. C., 397, 407, 443
Mitscherling, W. O., 266, 267, 966
Mitsukuri, S., 502
Mittasch, A., 186
Mitzengendler, S. F., 785
Mixon, L. W., 411
Mixter, W. G., 1283
Mizoshita, T., 136
Mizushima, S., 367
Mizuta, M., 31, 34, 35
Mnookin, N. M., 497, 507
Moedrickx, P., 773
Moehrle, E., 114, 130
Moelwyn-Hughes, E. A., 829
Moens, R., 267
Moerbeek, B. H., 925, 1176, 1184
Moesse, L., 844
Moffett, E., 516, 718
Moffitt, J. A., 1266
Mohn, A., 732
Mohr, U., 1035
Moissan, H., 711
Mokhnach, V. O., 511, 829
Moldavskii, B. L., 70, 73, 199, 484, 757, 930
Molinari, E., 242
Molitor, H., 528
Mommsen, E. Th., 465
Monakhova, V., 881
Moncrieff, R. W., 498, 581
Mondain-Monval, P., 1005, 1014
Monsanto Chemical Co., 330, 577, 605, 732, 778, 783, 794, 917, 918, 926, 945, 952, 958-960
Monsanto Petroleum Chemicals, Inc., 216
Monson, L. T., 1086
Montag, P. G., 1073
Montaigne, M., 767
Montgomery, H. A., 890
Montgomery, S. A., 45, 1204
Montgomery, W. B., 97, 99, 109, 116, 118-120
Monto, L., 621
Moor, H. H., 42
Moor, V. G., 144, 173, 174, 310, 357, 387, 650
Moore, G. V., 499, 518, 798
Moore, H., 28, 1034, 1117
Moore, R. J., 208
Moore, R. L., 220
Moore, W. A., 1279
Moose, J. E., 191
Moran, R. C., 815
Moravec, E. L., 1257
Moravec, R. Z., 161, 309, 386, 390, 392, 394-396, 635
Morehouse, F. R., 722
Moreton, H. H., 1220
Morgan, D., 933
Morgan, G. T., 40, 380
Morgan, J. J., 58, 59, 68, 149
Morgan, M. D., 1179
Morikawa, K., 1229, 1232, 1235, 1236
Morita, N., 273
Morley, J. F., 852
Morozov, K. A., 880
Morozov, V. V., 459
Morrell, J. C., 111, 133, 135, 136, 139, 143, 146, 244, 454, 455, 476, 478, 488-490, 614, 635, 636, 646, 665, 666, 668, 670, 907, 908, 912-914, 918-920, 922-924, 928, 929, 1034, 1035, 1044, 1045, 1058, 1064, 1199
Morris, H. E., 347-349
Morris, R. E., 588, 897
Morris, T. C., 249
Morrison, G. O., 717
Morschel, H., 422
Morse, L. S., 738
Mortensen, R. A., 1022
Morton, A. A., 827
Morton, J. M., 95, 103, 892
Morway, A. J., 1116
Moseley, F. J., 577
Moser, F. R., 115, 475, 477, 832, 930
Moses, F. G., 486
Moskovits, N., 889
Moskvin, G. M., 337
Moss, H., 911
Mótusz, J., 232
Motwani, D. C., 525
Moulds, L. de V., 852

Mountain Copper Co., Ltd., 1048
Mouratoff, C., 935
Moureu, C., 905, 907
Moureu, H., 547, 557, 642
Mousseron, M., 520
Moynot, H., 1030
Mrazek, S., 703
Mühlendyck, W., 928
Mueller, E., 1164, 1173
Müller, E., 495, 698
Müller, E. L., 487
Müller, G., 938
Müller, H., 935
Müller, J., 38, 39, 977, 1206, 1207
Müller, M., 481
Müller, O., 954
Müller, R., 718, 728, 935
Müller, W., 561
Müller-Cunradi, M., 169, 174, 210, 213, 255, 1018
Muench, E., 539
Münch, W., 1110
Mugdan, M., 711
Mulinos, G., 546
Muller, G., 856
Muller, G. P., 528
Muller, J. F., 1077
Muller, R., 417
Mulliken, S. P., 16, 1144, 1152, 1179
Mumm, O., 702
Mund, W., 267
Munday, J. C., 68, 149
Munro, J. A., 751
Munro, L. A., 288
Munro, W. P., 848, 872, 873
Murat, M., 775
Murata, Y., 1232, 1236, 1244
Muresanu, P. L., 518
Murgulescu, I. G., 1102
Murphy, G. B., 475, 912, 925, 1016, 1029, 1176, 1309, 1313
Murrill, P. I., 917
Musatov, K., 929
Muskat, I. E., 678, 685, 686, 807
Musser, R., 711
Muszkat, K., 1228
Myddleton, W. W., 1230, 1234, 1237-1239, 1244, 1248, 1251
Myers, L. D., 1070, 1071
Myers, W. A., 41, 433
Mžourek, J., 32, 34, 35

N

Nabuco de Araujo, C. E., Jr., 453, 1067
Naef, E. E., 465
Nagai, Y., 1036
Nagel, R. H., 448
Nagiev, A., 667, 928
Nakabayashi, M., 1035
Nakamura, M., 710
Nakashidze, B. M., 1126
Nametkin, S. S., 16, 38, 865, 876, 1092, 1094, 1095, 1151, 1154, 1191
Namikawa, T., 276
Naphtali, M., 1110, 1201
Nargund, K. S., 467, 720
Nash, A. W., 202, 256, 261, 632, 671, 758, 1025, 1026, 1034, 1173
Nash, C. W., 645
Nashan, P., 264, 882, 903
Nasumyan, V., 964
Natelson, S., 647, 825
National Aniline & Chemical Co., Inc., 487, 525, 946, 958, 960
National Oil Products Co., 1074, 1077, 1113
Naugatuck Chemical Co., 429
Naujoks, E., 443
Naumann, A., 844
Naylor, C. A., 989, 995
Nazarov, I. N., 87, 411
Nazarov, S. A., 376, 388, 1080
Nazarov, V. G., 174
Nazarova, Z., 402, 412
Neale, A. E. T., 619, 829
Nederbragt, G. W., 255
Neeley, A. W., 671
Nef, J. U., 1092
Neher, H. T., 527
Neild, H. W., 1261
Neilson, C. A., 1126
Neilson, H. R., 543
Neiman, M. B., 850, 872, 922, 981, 1009, 1123-1125, 1142
Neimark, O. M., 173, 389, 677
Neitzke, O. F., 1217
Nekrasov, A. S., 527
Nekrasov, V. V., 527
Nekrasov, Z., 1111
Nellensteyn, F. J., 1190, 1192, 1196
Nelson, A. F., 511
Nelson, E. F., 99, 104, 116, 117, 1170, 1205, 1307-1310, 1312-1314, 1316, 1323, 1325, 1329, 1331, 1333, 1334
Nelson, R. E., 752, 797
Nelson, R. F., 469, 1107
Nelson, W. L., 28, 1168
Nemiritzkii, B. G., 978
Nemirovich, M., 374
Nemtsova, Z. N., 651
Nemtzov, M. S., 95, 106, 107, 636, 639, 641, 643, 646, 1155
Nenitzescu, C. D., 90, 94, 185, 198, 205, 444, 445, 463, 472, 564, 612, 613, 767, 1099-1102, 1302
Neon Research of Conn., 266, 267, 966
Neptune, F. B., 1017, 1026
Nernst, W., 313, 1172, 1279
Nesmejanow, A. N., 887
Neukom, O. W., 1114
Neuman, E. W., 370
Neumann, J., 732
Neumann, L., 703, 704
Neumann, M., 994, 995, 997
Neut, G. van der, 1177
Neville, H. A., 1086
Nevitt, H. G., 1176
Newell, H. I., 151
Newell, I. L., 1176
Newitt, D. M., 845, 856, 866, 872, 942
Newman, E. L., 1172
Newmann, A. C. C., 852
Newsome, J. W., 71
Newton, L. V., 26
Neyman, E., 45, 1065
Niagara Smelting Corp., 730
Nicloux, M., 354, 1262
Nicodemus, O., 701, 718, 722
Nicolai, F., 539, 715
Nicolet, B. H., 474, 761
Niederl, J. B., 604, 1172
Nielson, H., 929
Nieuwland, J. A., 308, 376, 377, 383, 384, 403, 406, 423, 565, 596, 597, 603, 604, 607, 609, 680, 701, 704, 706, 708, 709, 711, 714, 715, 719, 722-724, 826, 903, 924, 1162
Nifontova, S. S., 16, 38, 1092
Nikhamov, I., 458
Nikiforov, L., 935
Nikiforov, V. K., 265
Nikitin, N. I., 558, 559, 745
Nikolaeva, L. I., 164, 1145
Nikol'skaya, V. P., 935
Nikolskii, M. S., 879
Nikolyuk, B. A., 793
Nilsson, H., 520
Nishi, I., 755, 756
Nisson, P. S., 478, 666
Nitardy, F. W., 337
Nitka, H., 461
Nixon, A. C., 826
Noack, K., 545
Nobel, J. W. le, 1192
Noll, A., 535
Noller, C. R., 764, 902
Norina, L. I., 1115
Norris, J. F., 62, 67, 385, 412, 413, 417, 783
Norrish, R. G. W., 438, 448-450, 845, 846, 870, 877
North, C. O., 542
North, C. W., 498, 581
Norton, F. H., 586, 588
Norton, R. H., 1148
Nott, W. B., 1266
Nottage, M., 37
Novotny, D. F., 1144
Nowak, A., 43
Nowlen, J. P., 571
Noyd, T. F. G., 1169
Noyes, W. A., Jr., 777
Nozawa, R., 1337
Nozicka, F., 778, 949, 964
Nuesslein, J., 583, 584
Nugey, A. L., 232
Nutt, D. B., 476
Nutting, H. S., 302, 550, 629, 716, 736, 752, 894
N. V. Machinerieen-en Apparaten Fabrieken "Meaf," 1200
N. V. Mijnbouw-en Cultuurmaatschappij "Boeten," 1192

O

Obenaus, W., 935
Oberbach, J., 1206
Oberfell, G. G., 24
Oberg, E., 343
Obergfell, P., 42
Oberhelman, H. A., 1260
Oberle, A., 232
Obermiller, M., 619
Oberschlesischer Berg- und Hüttenmänischer Verein E.v., 758
Obleukhova, O. S., 1175
Obryadchikov, S. N., 102, 104, 109, 111, 1192
Ocun, E. A., 113, 488
Oda, R., 55, 180
Odell, W. W., 190, 229, 250, 275, 276, 331, 471, 651, 870
Oehring, W., 1153
Oettingen, W. F. v., 538, 580, 681
Office central de chauffe rationnelle, 1161
Offutt, H. H., 247
Ogg, R. A., Jr., 502, 807
Ogura, S., 581
Ohse, 1221
Oil Institute of Baku, 328
Oil Utilities Co., 1047
Okamoto, G., 725
O'Kelly, A. A., 790
Okhapkina, N. F., 164
Okunevskii, I., 733
Olcott, H. S., 914
Oldham, B. C., 738
Olin, J. F., 807, 810
Olin, R. R., 577
Oliver, S. C. J., 805
Oliver, T. C., 464
Olivièro, M. J., 1000
Ollander, O., 319
Olsen, A. L., 369
Olsen, J. C., 731, 733

Olson, E. T., 342
Oosterhout, J. C. D., 476, 941
Oostveen, W., 229
Oparina, M. P., 840
Oppenheim, R., 111
Opryshek, J., 433
Oranienburger Chem. Fabrik. A.-G., 1076, 1084, 1118
Orelup, J. W., 576, 917, 918
Orlov, E. I., 1223, 1241
Orlov, N. A., 32, 483, 963, 971, 1161
Orlov, N. N., 208
Orlov, S. M., 643
Orlova, A. P., 687, 707
Orlova, N., 543
Ormandy, W. R., 369, 375, 376, 1035, 1165, 1185
Ornstein, L. S., 939, 940
Orshanskii, D. L., 253
Orzhekhovskii, V. V., 671
Osborn, R. T., 1070
Osborne, R. L., 546
Osburn, M. R., 891
Osenova, T., 1109
Osetrova, E. D., 565
O'Shea, K., 1261
Oshima, Y., 245
Oshuev, A. G., 782, 789
Osipova, V. P., 565
Osipovskii, B. Y., 674
Ospina-Racines, E., 654
Osterman, L., 788
Osterstrom, R. C., 213, 215, 657, 671, 928, 929
Ostrander, A. J., 126
Ostrovai, E. Y., 111, 143
Othmer, D. F., 501
Otsu, S., 998
Otsuka, H., 103, 140
Ott, C. J., 444
Ott, E., 466
Ottenhoff, P., 900
Otto, C., & Co. G. m. b. H., 459
Otto, F. C., 261
Otto, M., 210, 636, 674
Ouer, R. A., 549
Ovchinnikov, B. M., 271
Over, J., 203, 642
Overbaugh, W. V., 433, 453
Overstreet, R., 1280
Oxford, A. E., 580
Oxley, H. F., 422
Oyat'eva, G., 976

P

Paasche, W., 690
Pacyna, A., 1018
Padgett, F. W., 1170
Padovani, C., 27, 218, 224, 270, 274, 276, 870, 1241
Page, A. B. P., 557, 566
Page, J. M., 43, 434
Page, J. M., Jr., 38, 530
Pai, N. G., 554
Painter, R. K., 1220
Pajeau, R., 791
Palanyi, M., 826, 827
Palfray, L., 425, 766
Palfreeman, H., 953
Pall, D. B., 15
Palmer, L. S., 496
Palmer, W. G., 419
Paloma, M. H., 413
Pamfilov, A. V., 247
Paneth, F., 50
Pankov, G. A., 174
Panning, G., 1129, 1242
Panyatin, O. S., 1175
Panyutin, P., 32, 34, 907, 1153
Parini, V., 1155, 1199
Paris, A., 867
Park, C. R., 246
Park, J. G., 453
Parker, C. K., 938
Parker, E. P., 1258
Parker, H. E., 711
Parker, H. H., 831
Parker, J., 840
Parkes, G. D., 1095
Parkhomenko, V., 1069, 1105, 1112
Parkhurst, G. L., 732
Parks, G. S., 16, 101, 369, 415, 633, 642, 1225, 1271, 1274, 1276-1286, 1288-1290, 1300-1304
Parks, J. G., 404
Parks, W. G., 947
Parmalee, A. E., 829
Parmelee, H. M., 792
Parone, E., 718
Parrarano, N., 282, 319, 1034
Parrish, C. I., 50, 62, 63, 76, 78, 81, 83, 85
Parsons, J. B., 719
Pasiut, L., 627
Patat, F., 427, 883
Patco, Inc., 667
Patel, A. M., 959
Patent and Licensing Corp., 1074, 1116, 1217-1220
Patents Fuel and Color Corp., 917
Paterno, E., 711
Paterson Parchment Paper Co., 891
Patrick, J. C., 499, 528
Patrick, W. A., Jr., 929
Patrone, B., 253
Pattee, E. C., 15, 1333
Patterson, A. M., 695, 902, 903
Patterson, H. A., 1050
Patterson, J. A., 879
Patty, F. A., 405, 495, 528, 543, 556, 580
Paul, R. E., 58, 61, 66
Pauwels, J., 1095
Pavlov, B. T., 711
Pavlov, N., 90, 92
Pavlovich, P. I., 499
Pavlovskii, M. T., 1167
Pavolini, T., 1159
Payman, J. B., 583
Payman, W., 982
Payne, C. R., 929
Payne, E. H., 1175
Peairs, L. M., 1078
Pearce, J. N., 71
Pearce, S. J., 22, 1148, 1154
Pearce, T. J. P., 49, 56, 554
Pearl, W. A., 1002
Pearson, J. H., 792
Pearson, T. G., 449, 450, 720
Pease, R. N., 61, 95, 103, 555, 848, 872, 892, 1276
Peck, E. B., 1044
Peckham, S. F., 831
Peek, R. J., 326, 363, 364
Peel, J. B., 485, 720
Peletier, L. A., 1027, 1030
Pelton, E. L., 342, 407
Pelzer, H. L., 135
Pemberton, E. S., 424
Pembrey, M. S., 1261
Pendlebury, E. E., 575
Penhale, J., 1098
Penniman, W. B. D., 865, 963, 1050
Peoples, S. A., 1269
Peratoner, A., 711
Perelis, W. J., 747
Perkin, W. H., Jr., 699, 773, 775, 1111
Perkins, G. A., 176, 309, 389, 392, 528, 529, 568, 581, 704, 706, 716
Perkins, G. W., 425
Perkins, M. A., 830
Perkins, R. L., 486
Perkins, R. P., 418, 605, 818
Permatex Co., Inc., 539
Perrakis, N., 369
Perrin, M. W., 267
Perrins, T. S., 837
Perrot, R., 794
Perry, J. A., 280, 1048
Perry, J. H., 267, 1271, 1306, 1323, 1335, 1340, 1341
Perry, S. Z., 544
Persson, H., 710
Peski, A. J. van, 158, 175, 291, 323, 358, 364, 391, 392, 397, 420, 553, 929, 1016
Peter, E., 973
Peterkin, A. G., Jr., 41, 1044
Peters, K., 73, 131, 155, 177, 254, 256, 637, 704, 1252
Peterson, R. L., 440
Peterson, T. E., 568
Peterson, W. R., 1098
Petre, A. W., 546
Petrie, P. S., 302, 550, 716, 736, 752
Petřik, F., 256, 347
Petroleum Chemical Corp., 314, 356, 387
Petroleum Conversion Corp., 669
Petroleum Hydrogenation Co., Ltd., 112
Petroleum Processes Corp., 489
"Petrosani" Societate anonima Romana pentru exploatarea minelor de carbuni, 278
Petrov, A. A., 173, 347, 509, 520, 627
Petrov, A. D., 72, 87, 135, 137, 158, 202, 209-211, 258, 259, 261, 631, 643, 704, 823, 870, 1058, 1077, 1224
Petrov, G. S., 625, 964, 968, 969, 971, 1081, 1112
Petrov, G. V., 460
Petzold, F., 1125
Peukert, E., 971, 977
Pevere, E. F., 44, 215, 453, 478, 498, 499, 1017, 1018, 1056
Peyer, E., 94
Peyrot, P., 755
Pfaff, K., 560, 566
Pfeiffer, J. P., 1197, 1211
Pfeiffer, P., 628
Pflugk, H., 972
Pfund, A. H., 1180
Pfungst, A., 1096
Phatak, N. M., 1269
Philippon, M. L. A., 728, 745
Phillips, G. R., 1266
Phillips, J. G., 1176
Phillips, N. E., 201
Phillips Petroleum Co., 160, 191, 240, 268, 280, 460, 467, 470, 477-480, 489, 618, 656, 661, 926, 1098
Physical Chemistry Research Co., 136, 268
Picard, M., 1190
Pichler, H., 55, 155, 166, 168, 499, 703, 1224, 1239, 1241, 1244, 1246-1248, 1252
Pickard, R. H., 380
Picon, M., 722
Pidgeon, L. M., 219, 237, 239, 240, 1013
Pien, J., 452
Pier, M., 112, 186, 262, 671, 675, 1188, 1201, 1228
Pieters, H. A. J., 1038, 1156
Pietzsch, K. F., 952, 960

Piggott, H. A., 487, 559, 566, 583
Pignot, A., 980
Pigulevskii, V. V., 161, 323, 357, 387, 393, 899, 944
Pilat, S. v., 38, 39, 45, 977, 1065, 1071, 1190, 1200, 1201, 1207
Pilgrim, F. D., 62, 63
Pilo, C. W., 458
Pim, F. B., 417
Pimenov, V., 146
Pinchuk, S. E., 404
Pinck, L. A., 615
Pine, W. B., 314, 393, 593
Pines, H., 200, 208, 306, 489. 591, 592, 594, 596, 602, 634, 637, 640, 642
Ping, K., 136
Pinkel, I. I., 573
Pinkevich, Y. A., 41
Piontkowski, F. A., 629
Piotrovskii, K. B., 650
Piotrowski, W. J., 876
Pipik, O., 164, 323, 388, 618, 923
Pirlet, G., 896
Pirozhkov, N., 236
Pirrone, F., 451
Pirsch, J., 652
Pisarev, K. E., 461, 718
Pitman, A. L., 328, 710
Pitter, A. V., 743
Pittman, C. V., 1215, 1216
Pitzer, K. S., 1280
Pivovarova, S., 1075
Plakidina, V. A., 424, 714
Planckh, R., 38
Plant, J. H. G., 70, 883
Plaska, Kh., 567
Plate, A. F., 16, 90-92, 144, 171
Platen-Munters Refrigerating System Aktiebolag, 746
Platonov, M. S., 420, 424, 714, 850, 1091
Platonova, A., 248
Platz, C., 716
Plauson, H., 268, 634
Plentl, A. A., 1172
Pleshkova, S., 1413
Pletnev, K. N., 136
Pletz, V. M., 708
Plewes, A. C., 846, 896
Plisov, A. K., 846, 876, 963, 964, 973
Plotkin, Z. I., 346
Plotnikov, V. A., 953
Plummer, W. B., 656-658
Plyler, E. K., 367
Pochettino, A., 1198, 1206
Podbielniak, W. J., 599, 1138
Poe, J. G., 1258
Pöll, H., 43
Poetschke, P., 1019
Poffenberger, N., 14
Pohl, F., 1055, 1115
Pohl, W., 714
Pohland. R., 767
Poiseuille, 1173
Pokorny, O. S., 42, 1200
Pokorskii, V. N., 930
Poletaev, A. V., 643
Pollard, C. B., 583
Pollock, R. C., 43, 667
Polly, O. L., 71
Polonskaya, S. I., 668
Polyakin, Yu., 1149, 1151
Polyakova, I. M., 490
Polyakova, K. S., 565
Pomeraniec, J., 71, 72, 93
Pond. T. W. M., 369, 375, 1035, 1185
Ponte. G. de. 1066
Pool, W. O., 979
Poole, J. W., 38, 43
Poorten, A. C. ter, 204, 645
Pope, A. S., 727
Pope, J. C., 962, 972
Popov, A. A., 535, 554
Popov, M. A., 782
Popov, P. V., 556, 980
Popov, S. N., 103, 208, 668, 669
Popova, N. V., 135
Popova, V. A., 782
Poptzova, A., 728
Porteous, H. B., 727
Porter, A. T., 1047
Porter, C. A., 1311
Porter, F., 189, 279
Postovskii, I. Ya., 667, 928
Poth, E. J., 11
Potolovskii, L., 23, 144, 146. 203, 209
Potter, H., 473
Potts, G., 275
Potts, W., 535
Potts, W. M., 317
Pourbaix, M., 745
Powell, A. R., 458
Powell, L. S., 588
Pozhiltzeva, E. A., 135, 209, 211
Prahl, W., 779, 782, 786
Prater, A. N., 588, 897
Pratt, W. E., 18
Praudiere, E. L. A. E. de la, 450
Precoul, M., 1015
Pree, L. de, 730
Prélat, C. E., 425
Prelog, V., 583
Prerau, I., 241
Prettre, M., 992
Prevost, C., 697, 711
Price, H. W., 237
Price, R. H., 928
Prichett, C. G. F., 1214
Prickett, T. B., 126, 127
Priebs, B., 1095
Prik, E. M., 1098
Pring, J. N., 1283
Prins, H. J., 624, 811, 812
Pritchard, W. N., 191
Procter and Gamble Co. of Canada, Ltd., 1081
Proctor, A. C., 28
Prokof'ev, T. V., 103
Prokopchuk, N., 484
Prout, W. A., 1263
Prozumentik, M., 144
Prozumentik, R. S., 1105
Prudhomme, E. A., 126
Prutton, C. F., 758, 790, 825
Prutzman, P. W., 1106
Pryanishnikov, A. A., 443
Przemetzki, V., 613
Puchkov, P. V., 1145
Puchot, E., 508, 510
Pugachev, E. E., 793
Pugh, J. W., 874
Puig, J. J., 1247
Pukirev, A. G., 371
Pummerer, R., 901
Pungs, W., 212, 525, 970, 977, 1057
Punnett, E. B., 946
Purcell, R. H., 449
Purdue Research Foundation, 753, 766, 806, 1087
Pure Oil Co., 130, 160, 185, 189, 203, 212, 213, 215, 489, 636, 657, 665, 666, 671, 929
Puritan Soap Co., 546, 578
Purse, J. H., 568
Purser, J., 1116
Puryear, O. P., 1114
Pusl, P., 329
Putnam, M. E., 418, 783
Putnam, S. W., 9, 507, 790
Puttfarcken, H., 452
Putzillo, V. G., 1191
Puyal, J., 767
Puzitzkii, K. V., 699
P'yankov, V. A., 461
Pye, D. R., 1030
Pyhälä, E., 11, 179, 831-833, 1117
Pyhrr, W. A., 452
Pyman, F. L., 810
Pyzel, D., 169, 1018
Pyzel, F. M., 158

Q

Quandt, H. L., 576
Quandt Chemical Co., 576
Quanquin, B., 1014
Querfeld, D., 1035
Querfurth, W., 339, 422, 443
Quiggle, D., 32, 1032, 1033
Quill, L. L., 370
Quimby, O. T., 491

R

Rabald, E., 717, 718
Rabe, H., 212, 595
Rabinovich, A., 1109
Rabinovich, A. M., 1164
Rabinovich, A. Yu., 971
Rabinovich, E. I., 146, 178
Rabinovich, O. B., 1162
Racciu, G., 570
Rachkani, 1168
Radio Corp. of America, 542
Radjy, A. H. K., 48
Radulesco, G., 28, 518, 914, 924, 927, 1180
Rae, J., 538
Rafilzon, I. A., 172, 508, 510
Ragatz, E. G., 1043, 1205
Raginsky, B. B., 528
Rahn, F., 622, 623
Raineau, A., 352
Rakovskii, V. E., 1192
Rakusin, M., 17
Rall, H. T., 32, 180, 659, 1172
Ralston, A. W., 731, 979
Ramage, A. S., 190, 893
Ramage, W. D., 781, 1096
Raman, C. V., 1181
Ramayya, K. S., 758, 817, 1070, 1071, 1074
Ramchandani, C. N., 368
Ramsburg, C. J., 468
Ramser, H., 41, 727, 739
Rance, H. F., 896
Randall, M., 344, 1270-1272, 1274, 1293, 1296-1298, 1306
Randall, R. A., 1171
Raney, M., 1231
Ransom, H. K., 1257
Rao, S. R., 367
Raoult, E., 1214, 1218
Rapin, A., 483
Rapoport, I. B., 135, 144, 831, 1194, 1229, 1236, 1240
Raschig, F., G.m.b.H., 779, 782, 786
Rassweiler, G. M., 844, 1008, 1011-1013
Rathemacher, C. P., 753
Rather, J. B., 577, 915, 917, 918, 926
Rauert, H. P., 701
Ravdin, I. S., 528, 529
Ravikovich, A. M., 1155
Ray, A. B., 1049
Ray, A. C., 431
Ray, P. C., 431
Raymond, E., 572
Razderishin, 1069
Razumov, V. K., 260
Rechberg, A., G.m.b.H., 1075

Rector, E., 1018
Rector Gasifier Co., 1018
Reddish, W. T., 746, 1070, 1075-1077
Reder, R., 1246, 1247
Redgrove, E. P., 933
Redro Laboratories, Inc., 813
Reed, C. F., 756
Reed, F. C., 221
Reed, F. H., 733
Reed, R. M., 820, 1066
Rees, H. V., 490
Reeves, E. D., 976
Refiners Ltd., 490, 928
Regad, E. D., 496
Reiber, J., 1264
Reich, H., 171, 255
Reiche, A., 887
Reichert, J., 951
Reichert, J. S., 714, 719
Reichstein, T., 818
Reid, E. E., 471, 485, 592, 611, 763, 765, 769, 819, 1066, 1067, 1158
Reid, E. W., 379, 434, 495, 528, 567, 751
Reid, G. H., 435
Reiff, O. M., 577, 758, 817, 915, 917, 918, 926
Reilly, J. H., 156, 192, 301, 745, 783
Reilly, P. C., 232, 488
Reinbold, E. B., 237
Reinecke, H., 263, 264
Reiner, S., 970
Reiner, W., 1218
Reinhard, G. C., 790
Reinhardt, L., 1057
Reinhardt, R., 1167
Rembashevskii, A. G., 459
Remington, J. S., 1115
Remiz, E. K., 291, 357, 388
Remy, T. P., 487, 1112
Renaudie, M., 1038
Rendel, T. B., 1031
Rengade, F., 932
Renoll, M. W., 749
Renotte, J., 328
Reppe, W., 174, 715, 719
Reshchikov, P. M., 234
Resinous Products and Chemical Co., 818
Restelli, E., 342
Retailliau, E. R. P. E., 489
Retter, G., 1018
Reuss, F., 654
Reuter, R., 102, 105
Reyerson, L. H., 725, 750
Reynhart, A. F. A., 494
Reynolds, C., 1263, 1265
Reynolds, H. H., 736
Reynolds, R. J. W., 559
Reznichenko, M., 728
Rheiner, A., 700
Rheinische Kampfer-Fabrik G.m.b.H., 444, 448, 605
Rhenania Osrag Mineral Öl-werke A.-G., 261
Rhenania Verein. Chem. Fabr. A.-G., 465
Rhodes, E. O., 434
Rhodes, F. H., 39, 935
Rhodes-Perry-Martin, Inc., 732
Riboisiere, J. F. P. de la, 1017
Ricardo, H. R., 454
Rice, F. O., 50, 51, 53, 55, 67, 69, 71, 74, 79, 334, 425, 435, 436, 438, 440, 1016, 1096, 1102
Rice, K. K., 50, 51, 67, 69, 74, 79, 334
Rice, O. K., 636
Richardson, C., 1193
Richardson, R. S., 223, 242
Richfield Oil Co. of Calif., 668, 1214
Richman, E., 1151
Richter, G. H., 1104
Richter, V. von, 886
Riddick, J. A., 1080
Rideal, E. K., 51, 53, 55, 58, 61, 632, 634, 769
Rider, H. E., 1047
Rider, T. H., 480
Riebeck'sche Montanwerke A.-G., 973, 1057
Riedel, J. D.,—E. de Häen A.-G., 745
Riedelsberger, W., 254
Riegler, R., 946, 959
Riehm, 1206
Rigby, G. W., 412, 413, 417
Riggs, L. K., 1263
Riley, H. L., 852, 853, 895
Rimarski, W., 1264
Rings, J. D., 841
Rinkenbach, W. H., 496
Ripert, J., 538
Risi, J., 576, 647
Ritchie, A. V., 1145
Rittler, W., 782
Ritzenthaler, B., 617, 618
Rivkin, S. M., 447
Roadstrum, V. N., 1042
Roark, R. C., 376
Robbins, B. H., 1267, 1269
Roberti, G., 988, 1014, 1016, 1029, 1036
Roberts, C. H. M., 946, 969
Roberts, E. N., 927, 1071
Roberts, J. K., 163, 657
Roberts, O. E., Jr., 113
Robertson, D. W., 469, 1138, 1139
Robertson, L. H., 731
Robertson, R., 380
Robey, R. F., 245
Robinson, J., 529, 1105
Robinson, J. D., 604
Robinson, P. L., 485, 720
Robinzon, E. A., 1151, 1154
Roblin, R. O., Jr., 649
Rodgers, G. C., 1030
Rodman, C. J., 1195
Rodowskas, E. L., 425, 1096
Rodowsky, W., 611
Roduta, F. L., 942
Roediger, J. C., 1218
Roegiers, 261
Röhm and Haas A.-G., 527
Röhm and Haas Co., 347, 436, 448, 604, 605, 891
Roehrig, H., 486
Roelen, O., 1224, 1225, 1234, 1237
Roell, E., 192
Römer, E., 702
Roess, L. C., 37, 1319
Roessler and Hasslacher Chemical Co., 545, 710, 743
Rötger, H., 719
Rogers, A. O., 752, 797
Rogers, E., 434
Rogers, F. M., 489, 1106, 1191
Rogers, H. K., 231
Rogers, T. H., 913, 916-918, 927, 930, 933, 1190
Rogers, W. F., 456
Rohe, H., 758
Roka, K., 422, 423, 714
Rokhlin, S., 972, 973
Rokityanskii, I. V., 651
Rollefson, G. K., 555, 711, 887
Romanchuk, M. A., 701
Romashenko, P. I., 1073
Romberger, F. T., 1266
Romeyn, H., Jr., 1277, 1283
Romijn, H. M., 95, 191
Romstatt, G., 535
Roodenburg, N. M., 1192
Roper, T. D., Jr., 544
Rosanhoff, M. A., 1158
Rose, A., 32
Rose, B. L., 1043, 1204
Rose, F. W., Jr., 31, 33, 34, 36
Rose, W. G., 400, 775
Roseanu, I. R., 529, 987
Rosemberg, P., 171
Rosen, C., 964
Rosen, R., 398, 486, 938, 1072, 1138
Rosenberg, E. H. J., 41
Rosenberg, S., 334
Rosenburg, H. R., 818
Rosendahl, F., 99, 1224
Rosenmund, K. W., 604, 822
Rosenstein, L., 377, 378, 458, 489, 577, 1018
Rosenthal, S. M., 1262
Rosenthaler, L., 529
Rosenwald, R. H., 521, 531
Rosenzweig, J., 954
Rosinsky, W., 213, 671, 712
Rosljakova, E. N., 247
Ross, E. S., 1214
Ross, W. F., 437
Ross, W. H., 719
Rossetti, C., 254
Rossini, F. D., 13, 15, 30, 1277, 1280, 1282, 1283
Rossinskaya, I. M., 333, 421, 884, 885
Rossmann, E., 1152
Rosson, M. M., 215
Rost, T., 711
Rotenberg, I. A., 682, 684, 698, 706
Roth, A. W., 1277
Roth, O., 727
Roth, W., 261
Roth, W. A., 580
Rothmann, A., 569
Rothstein, B., 766, 770
Rotshtein, A. D., 517
Rovenstine, E. A., 1266-1268
Rowbotham, S., 1266
Rowland, H. R., 263
Rowsey, G. L., 476
Royama, G., 745
Rozanov, N. A., 763
Rozeboom, J., 729
Rozengart, M. I., 714
Rozhdestvenskii, B. A., 170
Rubanovskii, L., 650
Rubber Service Labs. Co., 890, 918
Ruberg, L. A., 561
Rubin, H. H., 1261
Rubin, L. C., 102, 106, 107, 1323, 1325, 1327
Rubina, L. B., 651
Rubinshtein, A. M., 92, 880
Rubztov, G. A., 1112
Rudakova, N. V., 357, 365
Rudder, F. P. I. de, 168
Ruddies, G. F., 1017
Rudenko, V. V., 912
Rudkovskii, D. M., 301
Rudneva, T. I., 558, 559, 745
Ruemele, T., 373
Rüsberg, F., 465
Ruff, O., 737
Ruhemann, S., 474
Ruhoff, J. R., 769, 1277, 1283, 1284
Ruhrchemie A.-G., 165, 168-170, 710, 1040, 1252, 1255
Ruibak, B. M., 1104, 1166, 1192
Ruigh, W. L., 528, 529
Ruimashevskaya, I., 559
Ruiz, I., 572
Rumbold, W. G., 27
Runtzo, P. M., 265

Runyan, A., 675
Russell, J., 722, 1040
Russell, R. H., 133
Russell, R. P., 276, 1298
Russell, W. F., 250
Rutherford, J. T., 42, 1105
Ruthruff, R. F., 151, 163, 631, 637, 640, 656, 657, 662
Ruttan, R. F., 549
Rutter, K., 964
Ruyer, A., 589
Ruzicka, L., 94, 185
Ryazanovskii, N., 1112
Ryazantzev, M. D., 711
Ryden, L. L., 617, 618, 724
Rydon, H. N., 318
Ryland, L. B., 1159
Rysselberge, M. van, 16

S

Saal, R. N. J., 41, 666, 1170, 1206
Sabanajeff, A., 711
Sabatier, P., 88, 645, 1094, 1223
Sabelnikov, E. D., 532
Sabetay, S., 575, 1151
Sabina, J. R., 1030
Sabrou, L. G., 1038
Sachanen, A., 99, 103, 106, 107, 109, 117, 1188
Sachanov, A., 1198
Sachs, A. P., 122
Sachsse, H., 55, 427, 883, 986
Sadgopal, 629
Sadovnikov, P., 986
Saenger, H., 825
Safonova, M. K., 175
Sage, B. H., 14-16, 1307, 1334, 1335, 1337, 1339, 1340
Sagel, H., 207
Sager, F., 668, 914
Sahay, V., 795
Saijo, S., 1035
Saint-Aunay, R. V. de, 89
Saint-Mars, J. de, 466
Sakano, S., 469
Sakellarios, E., 622, 1082
Sakhanov, A. N., 13, 23, 29, 31, 33, 38, 39, 908, 1150, 1184, 1190
Sakmin, P. K., 155, 163, 1128, 1142, 1143
Sakurada, I., 39
Sala, C. J., 575
Salceanu, C., 1001
Sallmann, R., 787
Salmi, E. J., 413
Salmoni, R., 1169
Salo, T., 413
Salomon, T., 930, 931, 940
Saltmarsh, O. D., 438
Salzberg, P. L., 529, 560, 822, 1059, 1098
Sameshima, H., 136
Sand, J., 583
Sanders, F. J., 284, 288, 1302
Sandhaas, W., 170
Sandkuhl, H., 444
Sandmeyer, T., 626, 627, 720
Sandonnini, C., 807
Sankowsky, N. A., 496
Sargent, L. E., 919
Sargent, N. A., 327, 364
Sarkisov, E. S., 1069
Sarnov, C., 1206
Sartain, P. J., 728
Sato, M., 533
Sattler, L., 761
Sauciuc, L., 137
Saurwein, K., 171, 719
Sauter, E., 563
Savage, J., 743
Savel'ev, A. I., 651, 1077, 1116
Savinova, V. K., 843, 1015
Sayers, R. R., 405, 495
Saytzeff, A., 452
Sazanoff, P. P., 1118
Scarlatescu, N., 463, 472, 564
Scattola, M., 721
Schaad, R. E., 281, 490, 614, 637, 642, 703, 1017
Schaafsma, A., 530
Schaafsma, J. G., 1334, 1335, 1339, 1340
Schaarschmidt, A., 445, 446, 621, 1243
Schacke, B., 427
Schacken, J. M. G. de, 743
Schade, W., 998
Schaefer, A. E., 803
Schaefer, R. A., 580
Schaeffer, E., 773
Schalch, J., 626
Scharff, M., 951
Scharmann, W. B., 574
Schaufelberger, 1138
Scheel, K., 1277
Scheer, W., 1168
Scheflan, L., 731, 733
Schellmann, M., 976
Scherer, O., 716
Schering-Kahlbaum A.-G., 422, 446, 550, 605, 606, 776, 895
Schestakow, P. J., 831, 832
Scheuermann, A., 712
Schicktanz, S. T., 31, 36, 40, 433, 547, 942, 1170
Schierholtz, O. J., 535, 547
Schiffler, H. J., 133, 134
Schiflett, C. H., 266, 703, 725
Schildwächter, H., 209, 593, 1149
Schilling, H., 169, 170, 254, 255
Schindhelm, H., 820
Schivazappa, M., 883
Schladebach, H., 1115
Schlecht, L., 719
Schlitt, J. L., 163
Schlubach, H. H., 537
Schlüter, H., 22, 1192
Schmalzhoffer, F. X., 624
Schmatolla, V. O., 1151
Schmeling, F., 472, 1161, 1164
Schmid, A., 1124, 1125
Schmidlin, J., 952
Schmidt, A. W., 1027, 1028, 1029, 1030
Schmidt, E., 1096
Schmidt, E. R., 1263, 1266, 1268
Schmidt, H., 71, 72, 93, 929
Schmidt, J., 620, 621
Schmidt, M. E. A., 743
Schmidt, O., 186, 558, 764
Schmidt, R., 272, 931
Schmidt-Kehl, L., 727, 743
Schmieden, W., 59
Schmitt, G., 1132
Schmitz, E., 1103, 1108, 1112, 1113, 1115
Schmitz, W. H., 1199, 1202
Schnauffer, K., 1006, 1012
Schneider, G., 577, 1112
Schneider, H. F., Jr., 1175
Schneider, H. G., 314
Schneider, V., 74, 76
Schnetka, M., 710
Schnurr, W., 604
Schöfer, A., 1094
Schöller, C., 558
Schoeller, W., 550, 606, 776
Schöllkopf, K., 605
Schöneberger, M. R., 992
Scholl, R., 209, 1094
Scholz, E., 525
Schoorl, N., 729
Schorger, A. W., 559
Schorlemmer, C., 750
Schornstein, W., 460
Schoruigin, P. P., 971
Schrader, O., 898
Schrauth, W., 409, 757
Schreiner, E., 1277
Schrenk, H. H., 22, 405, 528, 580, 1148, 1154
Schroeter, G., 721
Schröter, G. A., 619
Schuette, H. A., 375
Schuhardt, V. T., 842
Schuler, R., 322, 326, 604
Schultz, R. F., 410
Schultze, G. R., 99, 101, 684, 700, 1152, 1297
Schulz, F., 1161
Schulze, W. A., 11, 268, 456, 467, 470, 477-480, 489, 926, 1031, 1158
Schumacher, H. J., 711, 741, 848
Schumann, G., 331
Schuster, C., 431, 575
Schuster, F., 1010, 1129, 1242
Schustina, V. I., 964
Schutt, H. C., 106
Schwaderer, W. C., 1176
Schwaebel, F. X., 953
Schwander, P., 745
Schwartz, F., 1188, 1192, 1193
Schwarz, H., 938
Schwarz, R., 10
Schwarzenbach, G., 469
Schwegler, C. C., 731
Schweitzer, P. H., 1033, 1034
Schweitzer, W. K., 380
Schwenk, E., 446, 550, 895
Schweyer, H. E., 1206
Schwoerer, R. C., 728
Scorah, L. V. D., 427
Scott, N. D., 340, 613
Scott, T., 490, 928
Scott, W. B., 327
Scott, W. D., 550
Seaman, H., 996
Seaman, W., 472, 486
Sebastian, J. J. S., 1136
Sebastian, V. A., 1078
Seddon, R. V., 555
Seeber, F., 1030
Seeley, E. E., 731
Seeley, W. L., 112
Seer, C., 209
Seevers, M. H., 1267
Sefton, L. B., 371
Seguy, J. D., 458
Seib, J., 343
Seibel, C. W., 22
Seidel, C. F., 94, 185
Seiler, K., 48
Sekretareva, E. V., 442
Selden, H. M., 1257
Selden Co., 335, 915, 945, 946, 949, 950, 952, 954, 960
Selden Research and Engineering Corp., 958-960
Selheimer, C. W., 1323
Selivanova, N. L., 674
Sel'skii, L., 456
Semb, J., 772
Semon, W. L., 429
Semenov, 620
Semenov, N. N., 845, 995, 997, 998
Semenov, P. A., 83, 155, 172
Semerano, G., 332
Sen, S., 1229
Senden, G. H. van, 925
Senderens, J. B., 805, 806, 1094, 1223
Senitchenko, S. E., 458
Sennewald, K., 497
Sentzov, P. A., 1156

Seon, M., 71, 154, 273
Serbinov, A. I., 850, 872, 997
Serebryakova, E. K., 744
Sereda, J., 1065, 1068, 1071, 1074
Sergienko, S., 651
Serritella, A. F., 1261
Serruys, M., 1014, 1027
Seton, A., 1189
Seuseman, C. E., 942
Sever'anova, V. I., 93, 186
Sexauer, W., 190
Seyden, G. B., 158
Seyer, W. F., 17, 42
Seyferth, H., 1076
Seyler, H. W., 263
Seymour, G. W., 542, 818, 889
Shackell, L. F., 1267
Shaffer, S. A., 595
Shah, M. S., 467, 720
Shaikind, S. P., 850, 1091
Shakhnazarova, E. M., 92
Shaknovich, N. B., 1069
Shalaeva, T. V., 510, 753
Shankland, R. V., 671
Shannon, A., 581
Shapiro, U. G., 378
Shaposhnikov, V. G., 404
Shappirio, S., 755, 829
Sharp, B. B., 727
Sharp, W. E., 750, 751
Sharples Solvent Corp., 312, 390, 412, 513, 595, 604, 749, 751, 755, 807, 810
Sharples Specialty Co., 495, 745, 753
Shaverdova, E., 1104, 1109
Shaw, J. A., 458
Shaw, M. B., 566
Shawinigan Chemicals Ltd., 885
Shcheglova, A. P., 171
Shchigel'skaya, M., 493, 506, 783
Shchitikov, V. K., 909
Shchukarev, S. A., 461
Sheely, C. Q., 876, 881, 966
Sheinman, A. B., 124
Shell Development Co., 41, 115, 158, 161, 162, 169, 175, 214, 216, 221, 241, 249, 291, 293, 305, 309, 323, 325, 336, 346, 358, 364, 377, 386, 390 397, 408, 410, 417, 418, 420, 433, 443, 451, 457, 458, 462, 470, 472, 475-477, 486, 489, 494, 509, 510, 516, 518, 522, 523, 530, 544, 548, 553, 567, 589, 594, 604, 606, 627, 629, 635, 642, 657, 665, 672, 703, 712, 719, 750, 832, 841, 869, 889, 929, 930, 1017, 1018, 1061, 1073, 1112, 1205
Shell Petroleum Corp., 130, 929
Shelton, R., 480
Shenderova, R., 323
Shenderovich, I., 1155
Shenfinkel, I. K., 216
Shepherd, F. M. E., 1035
Shepherd, M., 1130, 1131
Sherbino, M. R., 1114
Sherborne, J. E., 15
Sheremet'eva, M. S., 651
Shereshevskaya, I. S., 466
Sherman, A., 491, 683
Sherman, H., 26
Sherman, W. O., 1259
Sherrill, M. L., 317, 318
Shevyakova, L., 1229, 1236
Shiffler, W. H., 283, 291, 362, 396, 397, 407, 443
Shildneck, P. P., 526
Shile, V. N., 1155
Shillenn, P. A., 542
Shilyaeva, L. V., 650
Shimomura, Y., 1039
Shinkle, S. D., 815
Shipp, V. L., 1104
Shipway, F. E., 528, 1264
Shiryaeva, G., 975
Shneider, F., 1069
Shoeld, M., 458
Shoemaker, B. H., 930, 933, 937, 1190
Shofner, L., 442
Shoholkin, K., 992
Shomate, C. H., 1279, 1283, 1284, 1291
Short, O. A., 580
Shoruigin, P. P., 559, 565, 631, 823, 824, 843, 877, 978, 1090
Shrenk, H. H., 1148
Shriner, R. L., 561, 839, 1155
Shtakelburg, I. I., 394
Shter, R. S., 709
Shtrom, D. A., 929
Shuikin, N. I., 31, 33, 92, 178, 179, 185, 346, 347
Shumilov, A. I., 144
Shusterovich, G. M., 730, 733
Shustina, V. I., 941
Shvedov, D. A., 975
Shvemberger, V. I., 164
Sibiryakova, G. N., 347
Sickman, D. V., 555, 636, 725
Sidersky, D., 327
Sidorenko, K., 620
Siebenbürger, H., 1084
Siebeneck, H., 1163, 1189
Siebeneicher, K., 300, 327
Siecke, W., 464
Siedler, V., 328, 329
Siever, C. H., 434
Siftar, I., 99
Signaigo, F. K., 1019, 1024
Signer, R., 1183
Sigwalt, R., 202, 466, 1177
Sikes, A. W., 1199
Silakov, S. M., 1117
Silica Gel Corp., 669
Simek, B. G., 229, 1193
Simon, W. E., 572
Simplex Refining Co., 832
Sims, C. J., 1097
Sinclair Refining Co., 135, 231, 353, 475, 675, 756, 928, 979
Singer, L., 1173
Singer, S. C., 142, 1033
Sirejols, A. P., 1039
Sise, L. F., 1266
Sivertz, C., 306
Sivova, A. N., 93, 186
Skarblom, K. E., 189, 534
Skelly Oil Co., 136
Skelton, W. E., 453, 495, 507, 513, 543, 546, 745, 789
Skirrow, F. W., 717
Sklianskaya, R. M., 424
Skornyakova, V. F., 537
Skosarewski, M., 711
Skowronski, F. J., 930
Skraup, S., 448
Skruipnikov, K. A., 1001
Slagle, W. M., 11
Slanina, S. J., 596
Sloane, R. G., 215, 758, 915, 918, 937
Sloane, R. W., 1002
Slobodin, Ya. M., 87, 88, 173, 347, 642, 650, 651, 824
Slooff, A., 1128
Slottman, G. V., 701
Slowter, E. E., 130
Sluys, P. W. van der, 397
Small, J. B., 1217
Smekal, A., 1181
Smeykal, K., 614
Smidovich, F., 111
Smiley, O., 1214
Smirnov, B., 840
Smirnov, N. I., 173-175
Smirnov, P., 1188
Smirnov, V. N., 540
Smirnova, A. I., 83, 172
Smirnova, Z. M., 270
Smith, A. D., 130
Smith, A. K., 790
Smith, A. O., Corp., 885
Smith, A. S., 1148
Smith, C. L., 130, 489
Smith, C. N., 249
Smith, D. F., 1225, 1227
Smith, F. B., 778
Smith, F. D., 958
Smith, F. L., 1015
Smith, G. F., 739
Smith, H. A., 1165, 1277, 1280, 1283, 1284
Smith, H. G., 215
Smith, H. H., 1175
Smith, H. M., 32, 180, 659, 905, 938, 1172
Smith, H. P., 777
Smith, H. V., 136
Smith, J. C., 318, 723
Smith, J. W., 1217
Smith, K. J., 136
Smith, L., 520
Smith, L. B., 878, 879
Smith, L. I., 208
Smith, L. R., 26
Smith, M. A., 925
Smith, M. P., 375
Smith, O. L., 190, 893
Smith, P. R., 1217, 1219
Smith, R. A., 403
Smith, R. L., 1322, 1323
Smith, T. A., 793
Smith, W. A., 669, 926, 930
Smith, W. F., 681
Smith, W. R., 82
Smithuysen, W. C. B., 364, 397
Smola, A., 574, 578, 587
Smolenski, K., 342, 638, 878
Smoots, J. P., 604, 917
Smyth, H. F., 733
Smyth, H. F., Jr., 731, 733
Snell, F. D., 193, 1220
Snider, L. C., 9, 19
Snow, H. R., 215
Snow, R. D., 22
Snyder, J. W., 245-247, 249, 251, 252
Snyder, L. J., 475
Soare, A. G., 526, 729
Sobecki, W., 772
Sobolev, B. N., 1161
Sobolev, I. A., 421, 714
Soc. A Klönne, 460
Soc. anon. carburanti Italia, 1039
Soc. anon. des carburants speciaux, 927
Soc. anon. le Carbone, 11
Soc. anon. Tokalon, 575
Soc. Carbochimique (Soc. anon.), 516-517, 533
Soc. des usines chimiques Rhone-Poulenc, 318, 588, 624, 916
Soc. d'études et realisation dite Ereal, 930
Soc. francaise de catalyse généralisée, 552, 586, 893
Soc. internationale des procèdes Prudhomme (S. I. P. P.) 126
Soc. pour l'ind. chim. à Bâle. 254, 577, 787, 891, 1084
Socony Vacuum Oil Co., 217, 291, 392, 577, 732, 758, 815, 817, 915, 917, 918, 926, 941, 1115
Sodermann, M. A., 527
Söll, J., 716
Sönke, H., 540

Sokolik, A., 992, 1007, 1010
Solodar, L. S., 208
Solodovnik, M. A., 758
Solokhin, L. A., 654, 700
Solomon, E., 334
Solonina, V., 616
Sommer, A., 1186
Sommer, W., 1057
Sonneborn, L., Sons, Inc., 530, 1073, 1074, 1219
Sorg, H. T., 198
Sorg, L. V., 926
Sorokin, V., 307, 699
Soroos, H., 15
Soskina, E. A., 636, 639, 641
Sosnina, A. S., 454
Sosnowski, S., 329
Soteria Chemische Fabrik A.-G., 819
Souders, M., Jr., 1323
Sowa, F. J., 308, 376, 377, 383, 384, 403, 596, 597, 603, 604, 607, 609, 724, 1162
Spahr, R. J., 724
Spalding, W. L., 279
Spangler, S. F., 464
Sparks, C. E., 797
Sparks, J. W., 1205, 1217
Sparling, D. W., 528
Spausta, F., 1039, 1185
Spear, E. B., 220
Speedy, A., 249
Speer, W., 432, 450
Speidel, W., 255
Spence, R., 877, 883
Spencer, R. C., 1002
Sperr, F. W., Jr., 465
Spielman, P. E., 1186, 1191, 1213
Spilker, A., 591
Spiltor, J., 1097
Spindler, H., 1039
Spondon, R., 889
Sponsel, K., 561
Sporer, F., 930
Sprake, C. H., 1006, 1023, 1026
Spring, F. S., 439
Spring, O., 315, 517, 1081
Spronck, S. J. H., 1156
Squibb, E. R., & Sons, 335, 336, 337, 528
Squires, L., 1173
Stadler, R., 169, 170, 254, 255, 705, 710
Stadnikoff, G., 13, 611
Staeger, H. C., 1195
Stagner, B. A., 28, 37, 434, 477, 668, 942, 1173
Stahly, E. E., 401
Staiger, F., 15
Stampe, G., 619
Stanco, Inc., 374, 453, 496
Standard Alcohol Co., 175, 305, 306, 322, 326, 345, 356, 359-362, 364, 365, 378, 389, 391-393, 396-398, 408, 420, 443, 635
Standard I. G. Co., 115, 255, 978, 1192
Standard Oil Co. of Calif., 42, 213, 283, 291, 362, 396, 397, 443, 457, 469, 471, 476, 486, 488, 672, 675, 832, 938, 1018, 1070, 1076, 1079, 1105, 1116
Standard Oil Co. of Ind., 44-46, 130, 163, 210, 212, 214, 215, 255, 256, 276, 380, 433, 434, 476, 489, 529, 530, 540, 575, 656-658, 662, 672, 732, 738, 746, 758, 809, 817, 818, 829, 915-918, 927, 937, 1018, 1033, 1071, 1075, 1078-1081, 1105, 1106, 1115, 1201, 1204, 1217, 1218
Standard Oil Co. of N. J., 356
Standard Oil Co. of Ohio, 136, 470, 486, 604, 659, 665, 916-918, 1043, 1046, 1204, 1205
Standard Oil Development Co., 36, 41, 42, 112, 132-134, 147, 149, 158, 159, 165, 168, 215, 219, 263, 275, 276, 278, 283, 292, 307, 313, 314, 333, 357, 358, 365, 372-374, 377, 397, 398, 407, 408, 414, 435, 436, 438, 441, 459, 469, 472, 477, 479, 480, 486, 489, 538, 575, 576, 595, 604, 611, 625, 636, 660, 661, 667, 672, 674, 727, 728, 731, 745, 746, 751, 756, 758, 814, 815, 865, 869, 874, 913, 915-919, 926-928, 930, 937, 938, 972, 976, 977-979, 1017, 1039, 1041, 1044, 1054, 1056, 1070, 1072, 1074, 1078-1080, 1082, 1086, 1097, 1112, 1114, 1116, 1189, 1200-1202, 1205, 1214
Stanley, H. M., 164, 175, 284, 285, 286, 292, 293, 294, 296, 322, 340, 671, 1121, 1138, 1302
Stansfield, R., 456, 1023, 1034, 1097, 1184
Stanton, G. T., 1029
Stanton, R. E., 263
Staples, M. L., 535, 547
Stark, A. R., 1184
Starkweather, H. W., 666
Staroverova, E. N., 173
Starr, J. V., 42, 746
Stastny, J., 327, 547
Staud, C. J., 496, 528
Staudinger, H., 15, 562, 617, 618, 647, 648, 700
Stauffer, C. H., 806
Stauffer Chemical Co., 730, 731
Staveley, L. A. K., 884
Stavrat, G., 112
Steacie, E. W. R., 334, 846, 851, 896, 897, 902, 1096
Stecher, J. L., 829
Steck, L. V., 712
Stegemeyer, L A., 1071
Stehman, C. J., 759
Steibelt, W., 979
Steigerwald C. 189
Steik, K. T., 575, 1064, 1077, 1113
Steimmig, G., 524, 557, 578
Stein, G., 652
Stein, O., 448
Steinbrecher, H., 18
Steiner, A. B., 267
Steiner, L., 1175
Steiner, W. L., 758
Steingroever, F. A., 783
Steinhofer, A., 647
Steininger, H. M., 667, 928, 1217
Steinitz, E. W., 1170
Steinkopf, W., 720
Stellwaag, A., 1221
Stepan, V., 583
Stepanek, J., 1090
Stephan, F. C., 545
Stephens, H. N., 907, 942
Stephenson, H. P., 160, 781
Sterman, S., & Co., 330
Stern, G., 679, 930
Stetser, J. B., 1148
Stevens, D. R., 488, 604, 929, 930
Stevens, J. R., 827
Stevens, P. G., 611
Stewart, L. C., 504, 710, 730
Stewart, R. M., 1063
Stewart, T. D., 492, 512
Stiles, S. A., 1266, 1257
Stille, H., 22
Stillman, T. B., 1170
Stirton, A. J., 786
Stobbe, H., 654
Stockdale, T. E., 758
Stockert, E., 665
Stockings, W. E., 871
Stockman, L. P., 26, 42
Stodola, F. H., 318
Stoermer, R., 647
Stoesser, S. M., 732
Stoesser, W. C., 778, 785
Stoicovici, E., 116
Stoll, M., 632
Stone, G. C. H., 820
Stone, H. G., 501
Storch, H. H., 52, 165, 167, 210, 636, 671, 733, 986
Storer, F. H., 17
Stormant, R. T., 427
Story, B. W., 486, 941, 1163
Story, L. G., 916, 917, 918
Stoughton, R. W., 1256
Stout, L. E., 732
Stowener, F., 732
Strahler, F., 299, 321, 322
Strange, E. H., 301, 307, 308
Stratford, R., 601
Stratford, R. K., 42, 112, 134, 1200, 1205
Stratford, W. M., 43, 44, 197, 666, 667, 669, 930
Strating, J., 31, 678, 688, 689, 694, 696
Straus, F., 510, 691, 693
Straus, J., 1079
Strauss, D. C., 1261
Strauss, R., 757, 759
Strebkov, V. D., 674
Strecker, A., 819
Strezynski, G. J., 578
Strigaleva, N. V., 650
Strizhevskii, I. I., 702
Strong, J. R., 1156
Strosacker, C. J., 159, 342, 407, 731
Struck, E., 822
Stuart, K. E., 324, 326
Stuart, M., 264
Stubbs, J. J., 942
Studien- und Verwertungs- G. m. b. H., 1234, 1238, 1249, 1253
Studinger, J., 823
Stüber, O., 1087
Stutzer, O., 18
Stuurman, J., 900
Style, D. W. G., 826
Subbotin, S. A., 674
Subkow, P., 530
Sucharda, E., 312, 431
Sudborough, J. J., 377, 1111
Sudfeldt & Co., 1074, 1105
Sürü, J., 48
Suess, H., 580
Sugawara, S., 728, 1337
Sugden, S., 482, 1180
Suida, H., 43, 938
Suirkin, Z. N., 793
Suiva, T., 1037
Suknarowski, S., 1070
Suknevich, I. F., 346, 453, 709
Sulflo Corp. of America, 469
Sulkow, P., 43
Sullivan, F. W., Jr., 130, 151, 212, 255, 380, 631, 637, 640, 656, 657, 746, 1018, 1201
Sullivan, P. H., 130
Sullivan, R. W., 783
Summerbell, R. K., 48, 581
Sumpter, M. C., 488
Sun, C. E., 301, 491, 614
Sunawala, S. D., 424
Sunen-Beneded, R., 1247
Sungalovskaya, L. R., 1069

Sun Oil Co., 45, 823, 1018, 1107, 1114
Susanov, Ya. S., 1107
Susemihl, W., 905, 906
Suslina, V. N., 490, 1044
Sussman, S., 547, 895
Suter, C. M., 343
Sutherland, G. B. B. M., 1182
Sutherland, H. S., 306
Sutherland, R. O., 491
Sutton, W. R., 39
Suwa, T., 1026, 1029, 1031
Suzuki, K., 905
Svanoe, H., 277, 433
Swallen, L. C., 422, 423, 443, 541
Swan, A., 375, 1037
Swann, A. J. E., 1325, 1327
Swann, S., Jr., 446, 452
Swann Research, Inc., 191, 193, 783
Swanson, H. R., 654-657, 659, 661
Swanson, P. F., 667
Swarts, F., 773-774
Sweeney, O. R., 863, 890
Sweeney, W. J., 1298
Swerissen, H. T., 1112
Swietoslawski, W., 354, 1285
Swift, C. E., 42, 46, 433, 1201
Swift, T. B., 1049
Swindler, C. H., 1259
Sydnor, H., 103, 106, 107, 109, 115, 118
Szankowski, W., 1065
Szayna, A., 73
Szegö, L., 1066
Szeszich, L. v., 907
Szigethy, L., 576
Szmigielska, J., 354
Szperl, L., 469

T

Taboury, F., 764, 770, 775
Taboury, M. F., 791
Taff, J. A., 18
Tait, T., 417
Takagi, Z., 1039
Takahashi, S., 533
Takebayashi, M., 315, 316
Takenaka, Y., 272, 755, 807, 817, 906, 937
Takens, E., 416
Takeuchi, O., 1096
Tallard, S., 425
Talley, S. K., 38
Tamaru, S., 714
Tamele, M. W., 889, 1159
Tanaka, Y., 714, 756, 758
Tanneberger, H., 170, 255, 677
Tanner, C. C., 461
Tar and Petroleum Process Co., 230
Tarasov, B. K., 142, 908, 912, 1164
Tarasov, G. Ya., 257, 262
Tarasov, P., 135
Tarasova, E. M., 91, 204, 445
Tarbell, D. S., 514
Tartakovskii, S. M., 499
Tartar, H. V., 820, 1066
Tatter, J. W., 539
Tausz, J., 254
Taveau, R. deM., 486, 533, 1018
Tawada, K., 998
Tawara, E., 1039
Taylor, E. G., 367
Taylor, E. McK., 19
Taylor, E. R., 415
Taylor, G. B., 169
Taylor, H., 711
Taylor, H. A., 704, 1096
Taylor, H. S., 50, 266, 273, 420, 1180, 1271, 1293, 1297
Taylor, I. B., 1266, 1268
Taylor, J. B., 52
Taylor, J. L., 932, 1173
Taylor, K., 1218
Taylor, R., 407
Taylor, R. S., 539
Taylor, S. S., 905, 938
Taylor, W., 807
Taylor, W. H., 473
Tchakirian, A., 728
Teichmann, C. F., 476, 490, 753, 1112
Teissl, L., 22
Telegraph Condenser Co. Ltd., 545
Tellegen, F., 549
Te Lou, C., 1027
Tenney, J., 1261
Teodoro, A. L., 1035, 1039
Ter-Akopova, M. A., 354, 1104
Terekhov, A. M., 442
Terent'ev, A. P., 654, 700
Terrel, H. T., 1114
Terres, E., 71, 72, 93, 461
Terry, A. G., 1214
Terry, J. B., 1184
Terteryan, A. B., 1103, 1105
Terzian, H. G., 146, 223, 280
Tettamanzi, A., 570, 571, 587
Teupel, E., 742
Teutsch, I., 484
Texaco Development Corp., 43, 44, 189, 191, 215, 433, 453, 469, 499, 636, 666, 667, 669, 916-918, 929, 941, 978, 1018, 1107, 1108, 1202
Texas Co., 27, 43-45, 112, 113, 134, 189, 190, 197, 223, 433, 434, 453, 469, 476, 478, 486-488, 490, 494, 495, 498, 506, 507, 513, 522, 533, 543, 546, 666, 667, 669, 671, 745, 756, 797, 801, 916-919, 930, 1017, 1018, 1044, 1056, 1105, 1107, 1110, 1112, 1114, 1116, 1205, 1214, 1218
Thacker, R. B., Jr., 475
Theberath, J., 460
Theimer, E. T., 563
Themsche, M. E. van, 710
Thermatomic Carbon Co., 220
Thiel, W., 691, 693
Thiele, E. W., 1172
Thiophene Products Co., 467, 1080
Thole, F. B., 37, 42, 550, 915, 1189
Thomas, C. A., 216, 412, 595, 604, 674, 807
Thomas, C. L., 57, 58, 61, 62, 64, 65, 66
Thomas, E. B., 422
Thomas, S. B., 1279, 1280, 1281, 1285, 1288, 1289, 1290, 1293
Thomas, W. H., 910, 913, 915, 1149, 1184
Thommen, H., 712
Thompson, C. L., 868, 1049
Thompson, G., 899
Thompson, H. W., 479, 554, 985
Thompson, J. K., 1011
Thompson, W. C., 11
Thomson, D. W., 368
Thomson, G., 62, 67
Thorn, S. D., 724
Thorpe, T. E., 371
Thurston, R. R., 1187, 1202, 1218
Tiba, K., 1096
Tidman, C. F., 319, 320
Tietig, C., 1118
Tietze, W., 251
Tijmstra, S., 130, 530, 929, 1205
Tikhomirova, M. M., 881
Tikhonov-Dubrovskii, N. T., 1154
Tilicheyev, M. D., 106, 117, 1150
Tillman, A. B., 732
Tiraspolsky, W., 1149
Tishchenko, D. V., 513, 783
Tishchenko, V. E., 338
Tishchenko, V. V., 971
Titani, T., 273, 794
Titman, H., 982
Toby, E. M., Jr., 1180
Todo, P., 45
Todd, S. S., 642, 663, 1279, 1283, 1284, 1291, 1300, 1301
Todd, W., 1076
Töhl, A., 208
Tokareva, K., 382, 402
Tolmachev, N. A., 808
Tolwinski, K., 22
Toma, V., 201
Tomasik, Z., 726
Tomkinson, M. G., 720
Tommila, E., 536
Tomonari, T., 430
Tompkins, D. H., 890
Tongberg, C. O., 32, 1032, 1033
Topchiev, A., 1090
Tops, J. L., 1027
Toul, F., 266, 703
Toussaint, W. J., 704, 716
Towne, C. C., 112, 113, 189, 190, 223, 666, 669, 917
Townend, D. T. A., 856, 866, 872, 873, 992, 995
Trakhtenberg, D. M., 94
Tramm, H., 168, 169, 170, 263, 281, 710
Trask, P. D., 19
Trautz, M., 90
Trautz, O. R., 1172
Travers, M. W., 49, 50, 56, 79, 89, 554, 1297
Traxler, R. N., 1206, 1215, 1216
Treibs, A., 12, 17, 20
Trent, W. R., 895
Tressler, D. K., 447, 1057
Treszczanowicz, E., 329
Tretolite Co., 577, 593, 946, 947, 969, 1074, 1075, 1086, 1114, 1116
Tret'yakov, V., 458
Triebs, W., 155
Trifel, A. G., 301
Trimble, H. M., 535, 1017, 1026, 1033
Trinidad Leaseholds, Ltd., 487, 1114
Triplex Safety Glass Co., 427
Troeller, W. J., 1179
Trojan Powder Co., 1090
Tronov, B. V., 768
Tropsch, H., 54, 56, 57, 58, 61-63, 65, 66, 78, 81, 83, 85, 157, 163, 166, 168, 699, 1132, 1135, 1142, 1147, 1223, 1224, 1227, 1228, 1242, 1244
Trout, H. H., 1261
Truchet, R., 729
Truffault, R., 592, 595, 645
Trumble, M. J., 112
Truog, E., 464
Trusty, A. W., 103, 105, 107, 108, 109, 145, 909
Try, A. G. L., 264
Tschenke, H. L., 711
Tscherniak, J., 1093, 1096
Tschunkur, E., 192, 480
Tseng, A. T. K., 540
Tseng, C. L., 505, 770, 824

Tsuneoka, S., 39, 1227, 1228, 1230, 1232, 1235, 1236, 1242-1244
Tsutsumi, S., 1224, 1229, 1230
Tucker, C. W., 248
Tucker, G. R., 248, 575
Tucker, R. P., 898, 1059, 1195
Tulleners, A. J., 202, 203, 300, 302, 303, 310, 642
Tuot, M., 311
Turner, H. G., 223
Turner, L. B., 480, 998
Turner, N. C., 24
Turner, S. D., 105, 1325
Turova-Polyak, M. B., 206, 540
Tuttle, M. H., 43
Tuyn, M. C., 300, 302, 303
Tweedle, H. C., 1189
Twining, R. H., 342
Twinn, C. R., 566
Twiss, D. F., 439, 619, 829
Twitchell, Process Co., 1070, 1071, 1076, 1077
Typke, K., 937, 940
Tyson, F., 722
Tyul'neva, A. F., 175
Tyulyukov, A., 461
Tyutyunnikov, B., 1113
Tzerkovnikov, I. M., 173, 175
Tzikin, S. P., 667, 928
Tzukervanik, I., 382, 401, 402, 411, 412
Tzurikov, F. F., 93
Tzyurikh, L. G., 681, 684, 705

U

Ubbelohde, A. R., 1015
Ubbelohde, L., 1173, 1174
Ubben, R. T., 604
Udrycki, A., 1068
Ueda, K., 1047
Ueda, Y., 1017
Ueno, M., 136
Ufer, H., 331
Ugryumov, P. G., 509, 519, 520, 588
Ulbricht, E. G., 538, 930, 1112
Ulich, H., 815
Ullrich, W., 134, 636, 666, 667
Ulrich, H., 458, 569, 575, 583, 584
Ulzer, F., 1113, 1117
Underwood, H. W., 823
Union Carbide and Carbon Corp., 223, 336, 377, 495, 544, 568, 586
Union Oil Co. of Calif., 42, 43, 189, 433, 529, 530, 538, 543, 575, 667, 710, 758, 832, 838, 918, 1043, 1107, 1109, 1114, 1201, 1204, 1205, 1218
United Carbon Co., 247, 248, 249
United Gas Improvement Co., 146, 223, 280, 1048
United Shoe Machinery Corp., 586
United States Rubber Co., 681
Universal Oil Products Co., 111, 115, 133, 135, 146, 157, 168, 213, 232, 241, 281, 434, 458, 471, 475, 476, 478, 488-490, 593, 595, 598, 605, 614, 625, 634-636, 646, 657, 662-666, 668-670, 741, 861, 914, 916-919, 926-930, 1017, 1043-1045, 1058, 1064, 1199, 1205
Uno, Y., 1206
Urazovs'kii, S. S., 1240
Urbain, G., 728
Urey, H. C., 50, 724
Urieva, F. E., 424
Urion, E., 772
Ursum, W., 738
Urushibara, Y., 315, 316
Ushakov, M. I., 421, 714
Ushakov, S. N., 717, 753
Usines de Melle (Soc. anon.), 159, 328, 339, 359, 391, 427, 516
Utsch, H., 773

V

Vacuum Oil Co., 486
Vacuum Oil Co. (Soc. anon. française), 731
Vagranskaya, L. I., 880
Vaidya, W. M., 896
Vail, W. E., 446, 626, 894
Vaile, T. B., 1266
Valentine, K. S., 476
Valik, I., 563
Valik, L., 563
Vallee, C., 710
Vallee, R. R., 513
Val'ter, S. F., 674
Van Amerigen-Haebler, Inc., 563
Vandendries, C., 517, 533
Vanderbilt, B. M., 1087, 1093, 1097, 1098
Vanderbilt, R. T., Co., 917
Van der Kloot, A., 727
Van Hook, A., 704
Van Horn, L., 1201
Vanier de Saint-Aunay, R., 257, 258, 259, 260
Vanillin-Fabrik G. m. b. H., 452
Van Name, R. G., 1271
Van Nuys, C. C., 161
Van Orstrand, C. E., 19
Van Rysselberghe, P., 940
Van Schaack, R. H., Jr., 409, 417, 433
Van Schaack Bros. Chemical Works, Inc., 305, 309, 359, 409, 417, 433, 626
Vansheidt, A. A., 290, 332, 353
Vantu, G. G., 445, 1100
Van Winkle, R., 335
Vapor Treating Processes, Inc., 668, 928, 929
Varet, R., 718
Varga, J., 1151
Varlamov, V., 971, 976, 977
Varma, P. S., 795
Varshavskii, S. L., 216, 609
Varvoglis, G. A., 1080
Vasilchakova, V. K., 831
Vasil'ev, A. A., 175
Vasil'ev, A. N., 38, 39
Vasil'ev, N. A., 1188
Vasil'ev, S. S., 54, 257
Vasil'eva, A. V., 931
Vasil'eva, O., 907
Vásquez, S., 424
Vaughn, T. H., 711, 722, 724, 826, 1162
Vaughn, W. E., 1277, 1280, 1283, 1284
Vayssieres, P., 566
Veal, C. B., 1023, 1029
Vegyipari és Kereskedelmi Kft. (Successor to Ferenc Harsayni), 1112
Veiler, M., 521
Veitch, F. P., 400
Velikovskaya, E., 1058
Velikovskii, A. S., 931, 1105
Velikovskii, D. S., 790
Vellinger, E., 15, 28, 914, 924, 927, 935, 937, 938, 1166, 1179, 1180, 1215
Velsicol Corp., 675, 1059
Veltistov, K. K., 714
Venkateswaran, S., 1183
Verdier, J., 1038
Verein. Chem. Fabrik, 465
Verein für Chem. Ind. A.-G., 715
Vereinigte Chemische Fabriken Kreidl, Heller & Co., 778, 950, 964
Verhoek, F. H., 554, 884
Verley, A., 401
Verona, R., 30, 1151, 1154
Versteeg, J. M., 530
Verstraete, E. I. K., 730
Verver, C. G., 41, 666, 1170, 1177
Vesselovsky, V. V., 1096
Vesterdal, H. G., 727, 977, 1070, 1082
Vickerstaff, T., 439
Vienne, G., 718
Vilbrandt, F. C., 863, 890
Vilikovsky, V., 327
Vinnikova, S. G., 185
Vinogradov, A. P., 46
Vinogradova, E. V., 700
Vinz, A. O., 41
Virabyantz, R. A., 13, 29
Virobyantz, R. A., 30, 31, 32, 1081, 1154
Vit, L., 370
Vittorf, N. von, 699
Vivian, D. L., 1066
Vlasova, E. A., 935
Vlodrop, C. van, 138, 179, 1154
Vlugter, J. C., 1035, 1154, 1177, 1179
Vobach, A. C., 231
Vogt, C. C., 576
Vogt, C. J., 26
Vogt, E., 788
Vogt, R. R., 265, 704, 722, 723, 724, 826, 903, 924
Voit, E., 1075
Volck, W. H., 434, 1077
Volhard, J., 1158
Vol'kenshtein, A. S., 507, 687, 707
Vol'kenshtein, F. F., 257
Volkhin, A. E., 960
Vollmer, W., 461
Vollrath, R. E., 435, 438
Volman, D. H., 1129
Volmar, 1152
Volnov, G. M., 337
Volnov, I., 431
Vol'nov, Y. N., 1229
Volzhinskii, I. A., 165, 171, 173, 389, 651, 677
Vonderwahl, E., 605
Voorhees, V., 163, 212, 255, 276, 433, 656, 671, 809, 829, 913, 916-919, 937, 1018, 1033
Voorhies, A., Jr., 1298
Voranov, F. N., 78, 172
Vorenko, M., 935
Voronkov, V., 1010
Voronov, A., 495, 745
Voronova, A. V., 78, 172
Vorozhtzov, N. N., 779, 782
Vorozhtzov, N. N., Jr., 782, 784, 785, 786, 789
Vos, J., 711
Vose, R. S., 669
Voznesenskii, A. A., 1069
Vuiborov, P., 229
Vuishelesskaya, N. S., 1114
Vuorela, A. A., 922
Vvedenskii, A. A., 185

W

Wacker, A., Ges. für elektrochemische Industrie G. m. b. H., 345, 434, 728, 731, 742
Wackher, R. C., 306
Wada, N., 533

Wade, W. H., 799
Wadsworth, J. M., 43, 667
Waerden, H. van der, 433
Wagnër, 1152
Wagner, C. R., 108, 160, 185, 203, 215, 636, 654-657, 659, 661, 662, 665, 666, 916
Wagner, E. C., 420
Wagner Electrical Corp., 542
Wagner, F. C., 819, 1067
Wainwright, G. E., 781
Wait, J. F., 113, 131, 929
Waite, C. P., 495, 543, 556, 580
Wakefield, C. C., & Co., Ltd., 938
Wakeman, R. L., 15, 16, 1144, 1152, 1179, 1183
Wal, M. J. van der, 890, 998
Walden, P., 12
Waldmann, E., 1074
Waldmüller, A., 1076
Waldner, M., 245
Waldo, J. H., 583
Walker, H. W., 915-918, 926
Walker, I. F., 866, 1128
Walker, J., 1230, 1234, 1237, 1238, 1244, 1248, 1251
Walker, J. C., 869, 872, 1049
Walker, W. H., 1173, 1335, 1340
Wallace, J., 870
Wallach, O., 621
Wallis, T., 329
Walter, C. M., 27, 1039
Walter, G. F., 317
Walter, H., 422, 423, 714, 715, 717
Walter, P., 1123-1125
Walther, C., 71, 72, 93, 1176
Walther, R., 1153
Walti, A., 549, 589
Walton, J. S., 1339, 1341
Walton, R. P., 1262
Walz, E., 353
Wandycz, D., 1206
Ward, A. L., 807, 1177, 1178
Ward, J. T., 41, 102, 106, 107, 631, 654, 658, 1323, 1325, 1327
Ward, K., Jr., 570
Wardner, G. A., 37
Warren, B. E., 245
Warren, C. M., 17
Warren, G. E., 415
Warren, G. W., 799
Warren, T. E., 193
Wartenburg, H. von, 1283
Was, D. A., 939
Washburn, E. R., 369
Washburn, E. W., 30, 36, 724, 1280
Wasserman, A., 441, 652
Wassermann, J., 290
Wasson, J. I., 915, 918
Watanabe, M., 728
Watanabe, S., 1229, 1232, 1235, 1236
Waterfill, R. W., 738
Waterman, H. I., 77, 138, 179, 202-204, 210, 216, 300, 302, 303, 310, 311, 642, 643, 645, 719, 1145, 1153, 1154, 1177, 1179
Waters, C. E., 435, 438
Waters, R. M., 1259, 1261, 1263, 1266-1269
Watson, C. B., 130
Watson, H. E., 22, 379
Watson, K. M., 1170, 1176, 1307-1310, 1312-1314, 1316, 1322, 1323, 1325, 1329, 1331, 1333, 1334
Watts, H. G., 163
Watts, S. S., 1007
Watts, V. E., 1218
Wawrzinoik, O., 1036
Weaver, J. B., 928
Webb, D. A., 354
Webber, C. S., 528
Webel, F., 579
Weber, A. P., 805
Weber, C. G., 566
Weber, G., 453
Weber, H., 1220
Weber, H. C., 103, 918, 1320, 1322, 1323, 1325
Weber, H. H., 710, 1154
Weber, H. M., 966
Weber, M. E., 1097
Weber, P., 740, 750, 752-754
Webster, H. G., 1018
Wei, T C., 296
Weibezahn, W., 717, 718
Weidenbaum, B., 492, 512
Weigelt, 790
Weigmann, H., 160, 189
Weihe, F. A., Jr., 532
Weiler, J., 1183
Weiler, J. F., 730
Weiner, N., 321, 1082
Weinstein, A., 727
Weinstein, O., 138
Weir, H. M., 1316, 1323, 1325, 1327, 1331
Weiser, H., 21, 40
Weiss, H., 935, 937, 940
Weiss, J., 473
Weissbach, H., 963, 977, 1057
Weisselberg, K., 935, 1161
Weissenborn, A., 565
Weith, W., 747
Weittenhiller, H., 464
Weitzenböck, R., 209
Welge, H. J., 296
Wellard, R., 1004, 1005, 1014
Weller, R., 909
Wells, A. A., 667, 928, 1202
Wells, J. H., 263
Welter, A., 1084
Wendehorst, E., 669, 1154
Wenker, H., 568
Wennett, J. W. G., 1018
Wenzel, F., 21, 40
Wenzel, W., 458
Wenzke, H. H., 715
Werde, H., 891
Werder, J. F., 434
Werner, A., 1094
Werner, E. A., 336, 377
Werner, R., 964
Wernick, S., 710
Wernicke, E. A., 1080
Werntz, J. H., 529, 566, 706, 825
Wertyporoch, E., 207, 753
Wesche, H., 720, 789, 825
Wesp, O., 1177
Wesson, L. G., 834
Westen, H. A. van, 1145, 1153, 1177, 1179
Westermann, W., 373
Westervelt, H. E., 543
Westfälisch-Anhaltische Sprengstoff A.-G., 546
Weston, P. E., 806
Westvaco Chlorine Products, Inc., 328
Whaley, F. R., 51
Wheeler, R. C., 1106
Wheeler, R. V., 81, 179, 180, 184, 185, 187, 631, 654, 984, 989, 995, 1000, 1001, 1005, 1011
Wheeler, T. S., 188, 525, 726
Whessoe Foundry & Engineering Co., Ltd., 194
Whetsel, R. V., 10
Whitaker, C. N., 1204
Whitaker, H., 489
Whitby, G. S., 92
White, A., 133, 165, 660
White, A. G., 98
White, A. H., 1170
White, E. C., 1240, 1262
White, G. S. J., 566
White, H. S., 1315
White, J. D., 30-34, 1155
White, N. R., 1030
White, R. V., 521
Whitehead, W., 434, 578
Whiteley, J. M., Jr., 42, 472, 661, 672, 998, 1041
Whitman, W. G., 1325
Whitmore, F. C., 15, 310, 318, 319, 400, 401, 411, 413, 645, 649, 726, 754, 759, 799, 895, 901
Whitmore, W. F., 355, 371
Whyte, S., 915
Wibaut, J. P., 95, 191, 306, 316, 716
Wiborg, F. B., 250
Wickert, J. N., 530, 587
Widenhorn, H. A., 1259
Wiebenga, E. H., 743
Wieclawek, B., 22
Wiedeking, K., 214, 814
Wieden, H. J., Jr., 226
Wiegand, W. B., 238, 245, 246, 248, 249, 251, 252
Wieland, H., 621-623, 697, 1082, 1094, 1264
Wiemann, J., 548
Wien, J. L., 1176
Wiesler, K., 713, 714, 889
Wietzel, G., 272, 275, 278, 712
Wietzel, R., 186
Wiezevich, P. J., 49, 59, 74, 152, 160, 179, 182, 435, 436, 438, 441, 479, 611, 659, 661, 672, 727, 731, 858, 860, 864, 867, 869, 874, 998, 1041
Wiggins, W. R., 37, 41, 48, 671, 758
Wiig, E. O., 505
Wijk, A. van der, 15
Wik, S. N., 282
Wilcox, W. D., 221, 225, 276, 277
Wild, W., 877
Wilder, H. K., 710
Wilderman, M., 511, 513
Wildshut, S. J., 876
Wildt, E., 613
Wiley, F. H., 538
Wiley, M., 190, 893
Wilhelm, R. H., 1091
Wilke, E., 228
Wilkie, W., 1018
Wilkin, R. E., 930
Wilkins, H., 1180
Wilkinson, P. D., 824
Wilkinson, W., 163, 283, 1025
Will & Baumer Candle Co., 543
Wille, R., 434
Willenborg, W. J., 1148
Willey, E. J. B., 259
Williams, C. L., 732
Williams, D., 342
Williams, D. B., 529
Williams, E. C., 336, 381, 417, 462, 486, 929
Williams, H. G., 686
Williams, I., 681, 706
Williams, J. S., 1123
Williams, J. W., 423, 438, 442
Williams, K. A., 1164
Williams, M., 1104
Williams, N., 122, 1033
Williams, R., 279
Williams, R. R., 357
Williams, T. B., 280
Williams, V. V., 622
Williams, W. H., 191, 192

Willien, L. J., 222, 280
Willig, E., 710
Willihnganz, E. A., 1174
Willingham, C. B., 37
Willink, H. D. T., 95, 191
Willson, C. O., 655, 1213
Willstätter, R., 559, 761-763
Wilson, A. L., 584, 809, 810
Wilson, A. M., 373, 408
Wilson, C. E., 547
Wilson, C. P., Jr., 604, 671, 915, 916, 924
Wilson, C. W., 1128
Wilson, D. M., 1213
Wilson, E., 49, 50, 74, 76, 79, 81, 83, 84, 88, 89, 166, 187
Wilson, F. P., 272
Wilson, J., 427
Wilson, J. L., 683
Wilson, M. M., 513, 755
Wilson, R. E., 41, 656, 657, 916, 918, 927, 1169, 1201
Wilson, S. D., 729
Wilson, W. S., 305, 327, 364
Winand, P., 1098
Winbladh, R., 1144
Windus, W., 526
Wingett, J. N., 1098
Wingfoot Corp., 464, 497, 916
Winkler, C. A., 427, 554, 884
Winkler, F., 55, 78, 115, 134, 158-160, 172, 263, 639, 665, 892
Winkler, J., 876, 1191
Winkler, K., 90
Winning, C., 147, 917, 919, 1054
Winstein, S., 510, 1147
Winter, R. M., 716
Winthrop Chemical Co., 565, 789
Wintsch, V., 1218
Winzer, K., 73, 131, 155, 177, 637, 1252
Wirtel, A. F., 577, 1075, 1086, 1114, 1116
Wirth, C., III, 454, 475, 912, 927, 1016, 1156, 1170
Wirth, W., 580
Wischin, R., 1107, 1173
Wiseman, P., 670
Wiseman, P. K., 670
Witherington, P., 1095
Withrow, J. R., 130
Withrow, L., 844, 1008, 1011, 1012, 1013
Witt, R. K., 1280
Wittfeld, C., 613
Wittich, E., 22
Wittig, G., 633
Wittka, F., 1166
Wittmeyer, H., 1104
Wittwer, M., 524, 557, 558, 562
Witzel, H. W., 960
Woerner, A., 535
Wohl, A., 946
Wohlberg, C., 570
Wojeichowski, M., 331
Wolf, A., 1214
Wolf, B., 794
Wolf, K., 260, 261
Wolfe, H. J., 250
Wolff, G., 731
Wolff, W., 679, 715
Wood, B. J., 769
Wood, C. E., 48
Wood, R. T., 731
Wood, W. L., 81, 187
Wood, W. R., 573
Woodbridge, P. D., 1266
Woodburn, H. M., 413, 799
Woodbury, C. A., 622
Woodhouse, D. L., 209
Woodhouse, J. C., 278, 279, 626, 871, 894, 1050
Woodrow, W. A., 1184
Woods, G. M., 42, 262, 457, 481, 1054
Woodward, J. O., 808
Woodward, R. E., 459
Woog, P., 466, 910, 911, 1176, 1177
Woolcock, J. W., 359, 421
Worstall, R. A., 1094
Worster, F. J., 390
Worton, N. G., 924
Wrether, W. E., 19
Wright, C. H., 304
Wright, E. C., 151
Wright, R. E., 787, 810
Wuertz, A. J., 787
Wulff, C., 158, 605
Wulff, R. G., 54, 168, 169
Wulff Process Co., 168
Wunderly, H. L., 597
Wunsch, J. A., 1108
Wurster, C., 1096
Wuyts, H., 889
Wyler, J., 1090
Wyman, J. B., 489

Y

Yakimkin, N. A., 1240
Yakubovich, S., 147
Yamada, T., 905, 937
Yamaguchi, S., 710, 805
Yamamoto, K., 54, 167, 180
Yamasaki, S., 794
Yamazaki, B., 747
Yannaquis, 38, 977
Yannu, Yu. G., 705
Yant, W. P., 22, 466, 495, 528, 543, 556, 580, 733, 980, 989, 1138, 1148, 1154
Yanuisheva, Z. S., 339
Yarzhemskaya, E. J., 944
Yavorskaya, E. V., 948
Yoder, P., 400
Yoshikawa, K., 866
Yost, D. M., 296
Youell, J. E., 284, 286, 292, 293, 296, 1302
Youker, M. A., 733, 735, 736, 737, 747
Youker, M. P., 460, 656
Young, C., 733
Young, C. A., 723, 903, 924
Young, C. O., 171, 435, 581, 586, 871, 878
Young, H. B., 223
Young, H. D., 305, 566
Young, H. S., 362, 393
Young, P. L., 314
Young, W., 424
Young, W. G., 372, 510, 889, 1146, 1147
Youtz, M. A., 163, 732
Yovanovitch, A., 1262
Yukhovskii, G., 972, 973
Yule, S. A. C., 924
Yumoto, K., 1001
Yur'ev, Yu. K., 29, 33, 185, 463, 484, 488
Yuster, S. T., 725, 750

Z

Zabel, M., 558
Zabolotzkii, T. V., 54, 227
Zaborovskaya, V., 1151
Zadolin, S. A., 668
Zaganiaris, J. N., 1080
Zahn & Co. G. m. b. H., 861
Zal'kind, Yu. S., 96, 405, 708, 722, 828, 945
Zalogin, N. G., 258
Zamfirescu, T., 922
Zanetti, J. E., 725
Zangirolami, A., 423
Zapf, L., 1107
Zappert, R., 424
Zappi, E. V., 342, 728
Zarkin, M. M., 1114
Zeberg, E. F., 807
Zeise, 628
Zeisenheim, F. C., 1047
Zelenin, N. I., 196
Zelikov, I. S., 1162
Zelinskii, N. D., 16, 29, 31, 33, 36, 90-93, 143, 172, 178, 179, 185, 195, 204, 206, 421, 445, 488, 714, 764, 770, 772, 775, 1099
Zellhoefer, G. F., 545, 549, 727, 738, 790
Zellman, R., 783
Zel'tzburg, A. I., 963
Zerbe, C., 36, 957, 1000
Zharkova, V. R., 185
Zhavornokov, P. V., 709
Zhavoronkov, N. M., 234
Zhegis, M. K., 651
Zherdeva, L. E., 38, 39, 211, 975
Zherko, A. V., 70, 72, 338, 878
Zhigalin, Ya. L., 174
Zhirnova, L. V., 1188
Zhukov, A., 851
Zhukov, I. I., 674
Zickermann, J., 1076
Zieber, B., 1171
Ziegenhain, W. T., 26, 41, 1032
Ziegler, K., 651, 698
Zieley, J. D., 1056
Ziese, W., 560
Zilberman, G. B., 147, 779, 782
Zimakov, P., 558
Zimmer, J. C., 674, 758
Zimmerman, G. B., 116
Zimmerman, P. W., 1256
Zingerevich, T. L., 674
Ziurys, E. J., 1035
Zlatogurskii, A. V., 651, 1116
ZoBell, C. E., 19
Zobel, F., 171, 255
Zolotarev, S. S., 164, 945
Zorn, H., 212, 213, 671
Zudilov, I. E., 196
Zurcher, P., 111
Zuydewijn, E. de R. van, 695, 696
Zvoruikina, V. K., 865
Zweig, W., 1155
Zwergal, A., 1155, 1200

Subject Index

A

Abietates, in coating compositions, 543
Abietic acid esters, emulsifying agents for asphalts, 1217
Absorbefacient, definition of, 746
Absorption, infra-red by hydrocarbons, 32
Acenaphthalene, benzene from, 946
—, maleic acid from, 946
Acenaphthene, acenaphthene-quinone from, 955
—, acenaphthylene from, 955
—, dehydrogenation of, 955
—, from propane, 182
—, naphthalic acid from, 955
—, naphthalic anhydride from, 955
—, oxidation of, 946, 955
Acenaphthenequinone, from acenaphthene, 955
Acenaphthenes, from propane, 61
Acenaphthylene, from acenaphthene, 955
—, from natural gas, 240
—, in Thermatomic process, 220
Acetal from ethyl alcohol, 338
Acetaldehyde, acetic acid from, 885, 889
—, acetic anhydride from, 885
—, acetone from, 421-423
—, acetoxime from, 886
—, as insecticide, 891
—, azeotropic mixture with isopropyl alcohol, 369
—, butanol from, 340
—, butyl acetate from, 340
—, butyl propionate from, 340
—, by oxidation of hydrocarbons, 868
—, — of olefins, 893, 896, 897
—, 2-chloro-1,3-butadiene from, 680
—, condensation of, 889
—, crotonaldehyde from, 878, 889
—, decomposition of, 883, 884
—, dimethyl-*p*-dioxane from, 579
—, effect of ethylene oxide on decomposition of, 555
—, effect on ignition temperatures, 992, 993, 994
—, free energy of formation, effect of temperature on, 1304
—, from acetylene, 253, 702, 712, 903
—, from butane, 863
—, from ethane, 856, 857, 872
—, from ether, 335
—, from ethyl alcohol, 337-340, 844, 848, 849, 872, 878, 879
—, from ethylene dichloride, 533
—, from ethylidene diacetate, 718
—, from kerosene, 860, 946
—, from methane, 264, 883
—, from methyl ethyl ketone, 449
—, from morpholine vinyl ether, 585
—, from polypropene sulphone, 618
—, from potassium ethylene trichloroplatinate monohydrate, 628
—, from propane, 862
—, from propene, 553
—, in butadiene, 175
—, oxidation of, 851, 885, 889, 899
—, ozonization of, 887
—, paraldehyde from, 886
—, reaction with acetylene, 680
—, — cracked distillates, 625
—, — 2-methylpyridine, 623
—, removal from butadiene, 175
—, use in ethylene oxidation, 896
—, — refining, 625
Acetaldol, 1,3-butene glycol from, 547
Acetals, ethers from, 715
—, from acetylene, 714
Acetals, from ether, 715
—, pyrolysis of, 341
Acetanilide, use in asphalt emulsion, 1219
Acetates, as solvents, 404, 405
Acetic acid, acetone from, 423
—, catalyst, dehydration of tertiary alcohols, 410
—, —, hydration of higher olefins, 297, 410
—, dehydration of, 501, 507
—, effect on esterification of olefins, 317, 318
—, from acetaldehyde, 885, 889
—, from acetone and air, 432
—, from acetone, steam and carbon monoxide, 432
—, from acetylene, 253, 713, 903, 904
—, from butane, 859
—, from carbon monoxide and hydrogen, 1244
—, from carbyl sulphate, 1081
—, from chloroethyl methyl ketone, 451
—, from cracking gas, 881
—, from dichlorobutane, 452
—, from ethane, 856, 857, 858
—, from ether, 335
—, from ethyl alcohol, 338, 339, 421, 844
—, from ethyl chloride, 830
—, from ethylene, 629, 893, 897
—, from formaldehyde, 889
—, from isopropyl alcohol, 371
—, from kerosene, 946
—, from mesitylene, 954
—, from methane, 870
—, from methylethylacetylene, 904
—, from methyl ethyl ketone, 450
—, from methyl isopropyl ketone, 450
—, from natural gas, 23
—, from paraffin wax, 971
—, from propane, 858, 859
—, from propene, 553
—, in cleaning agents, 1084
—, in distillation of petroleum, 34
—, ketene from, 436
—, reaction with acetylene, 717
—, — alkylacetylenes, 722
—, — *n*-butenes, 312, 314
—, — *ter*-butyl alcohol, 412
—, — cyclohexanol, 405
—, — diisopronyl ether, 377
—, — ethylacetylene, 718
—, — ethylene glycol, 540
—, — heptyl alcohol, 406
—, — isopropyl alcohol, 376, 1080, 1081
—, — ketene, 435
—, — methylcyclohexanol, 406
—, — *n*-pentenes, 313
—, — propene, 307, 308
—, — toluene, 448
—, — vinylacetylene, 706
—, sulphated, preparation of, 1086
—, use in emulsification of asphalts, 1220
—, — oxidation of methyl ethyl ketone, 450
—, — oxidation of paraffin wax, 973
—, — refining, 625
—, — separation of acids, 977
—, — isononane, 33
Acetic anhydride, 4-chloroacetophenone from, 789
—, from acetaldehyde, 885
—, from acetic acid-ketene reaction, 35
—, from ethylene glycol diacetate, 540
—, from ethylidene diacetate, 718
—, from ketene-benzamide reaction, 438
—, ketene from, 436
—, nitration of, 1090

Acetic anhydride, reaction with benzyl chloride, 794
—, — 2-butene and formaldehyde, 624
—, — chlorobenzene, 789
—, — hexamethylenetetramine, 888
—, — oleum, 1086
—, — polymethylene alcohols, 1118, 1119
Acetoacetanilide, from diketene, 442
p-Acetobenzoic acid, preparation of, 902
1-Aceto-3-butyrolactone, formation of, 565
Acetonaphthone, reaction with sulphur, 469
Acetone, amines from, 428
—, azeotropic mixture with isopropyl alcohol, 369
—, by oxidation of hydrocarbons, 868
—, by-product of reduction of aldehydes, 372
—, carboxylic acids from, 432
—, catalyst, esterification of styrene, 311
—, decomposition mechanism of, 425, 426
—, detection of, 373, 424
—, effect on absorption of propene by sulphuric acid, 357
—, estimation of, 424, 425
—, extraction of asphalts with, 1193
—, — carbon black with, 251
—, — naphthenates, 1105
—, — polyprene, 681
—, — resins with, 1188
—, — sulphonates, 1070, 1071
—, — vaseline with, 40
—, flocculating agent for asphalts, 1196
—, free radicals from, 427
—, from acetaldehyde, 421-423
—, from acetic acid, 423
—, from acetylene, 423, 714
—, from acetylphthalimide, 423
—, from butane, 863
—, from diethyl ether, 422
—, from ethyl acetate, 421
—, from ethyl alcohol, 337, 340, 421, 422
—, from ethylene oxidation, 897
—, from isopropyl alcohol, 370, 375, 420, 878
—, from isopropyl hydroperoxide, 382
—, from kerosene, 860, 946
—, from mesityl oxide, 423
—, from 2-methylpropene, 622
—, from propane, 858
—, from propene, 173, 292
—, in ethyl alcohol, 327
—, inflammability limits of, 980, 981
—, isopropyl alcohol from, 570
—, ketene from, 434
—, mesityl oxide from, 878
—, nitration of, 1090
—, oxidation of, 432, 853
—, phorone from, 878
—, photochemical decomposition of, 450
—, physical constants of, 424
—, pyrolysis of, 425, 426
—, pyruvic aldehyde from, 853
—, reaction with amines, 428
—, — ammonia, 428
—, — bromine, 430
—, — butyl alcohol, 443
—, — chlorine, 430
—, — ethyl alcohol, 443
—, — ethylhexaldehyde, 443
—, — ethyl methyl ketone, 433
—, — hydrogen, 432
—, — iodine, 430
—, — methyl alcohol, 443
—, — N-phenyl-β-naphthylamine, 429
—, — vinylethinylmagnesium bromide, 708
—, removal from acetylene, 1264
—, removal of diacetylene from, 170
—, solvent for acetylene, 169
—, — asphalt, 434
—, — butadiene, 174
—, — cellulose acetate, 434
—, — diacetylene, 170
—, — tar, 434
—, toxicity of, 424
—, use as blending agent, 1035
—, — fuel, 433
Acetone, use in desulphurizing hydrocarbons, 434
—, — dewaxing lubricants, 433
—, — estimation of paraffin wax, 1155, 1156
—, — extraction of petrolatum, 37
—, — motor fuels, 1039
—, — paint removers, 433, 790
—, — precipitation of asphalt, 935
—, — precipitation of asphaltenes, 1192
—, — removal of acetylene from gas mixtures, 171
—, — removal of olefins from mineral oils, 434
—, — removal of unsaturates from acetylene, 170
—, — rubber cement, 374
—, — separation of oil from wax, 495
—, — smokeless powder, 433
—, — storing acetylene, 433, 701
—, — synthetic resins, 433
Acetone anil, antioxidant for gasoline, 918
Acetone cyanohydrin, from acetone, 427, 428
—, α-hydroxy acid esters from, 428
Acetone-diacetone alcohol system, free energy changes in, 427
Acetone-gasoline blends, as motor fuels, 1038, 1039
Acetone peroxide, from oxidation of acetone, 432
Acetonylacetone, formation of, 425
Acetophenone, atropic acid from, 451
—, from ketene-benzene reaction, 439
—, oxidation of, 450, 853
—, phenyl glyoxal from, 853
—, preparation of, 943
—, use in dewaxing lubricants, 453
—, — polyprene, 681
Acetothienone, formation of, 611
Acetoxime from acetaldehyde, 886
Acetylacetone, as antiknock, 1018
—, effect on autoxidation of 1,4-dimethylcyclohexane, 907
Acetylcyclohexane, from cyclohexane, 1101
Acetyl chloride, from ketene-hydrogen chloride reaction, 439
—, from methyl chloride, 727
—, motor fuel from, 501, 1039
—, reaction with alkylacetylenes, 724
—, — benzine, 1099
—, — *ter*-butyl alcohol, 412
—, — cyclohexane, 204, 1101
—, — cyclopentene, 613
—, — *n*-hexane, 45
—, — methylcyclopentene, 205
—, — naphthalene, 447
—, — olefins, 611, 612
—, — pentane, 444, 1099
—, — thiophene, 611
—, — trichloroacetyl glycol, 541
Acetylene, absorption by acetone, 255
—, — alcohol, 255
—, — liquefied ammonia, 169
—, — sulphur dioxide, 169
—, acetaldehyde from, 253, 903
—, acetic acid from 253, 713, 903, 904
—, acetone from, 423
—, acetone, solvent for, 169
—, action of glow discharge on, 263
—, — iron arc on, 264
—, — mercury arc on, 264, 266
—, — silent discharge on, 258
—, — sunlight on, 264
—, — ultraviolet light on, 266
—, action on iodo-silver benzoate, 711
—, aromatics from, 89
—, as anesthetic, 1256, 1264
—, benzene from, 266
—, butenyne from, 89
—, butyro-lactone solvent for, 169
—, by electrical cracking of hydrocarbons, 131
—, carbon black from, 223, 235
—, carbon disulphide from, 467
—, chemical properties of, 701
—, chlorene from, 89
—, 2-chloro-1,3-butadiene from, 680
—, combustion of, 52, 1001, 1003, 1004
—, cuprene from, 704
—, cyclohexanone solvent for, 169

Acetylene, decomposition of, 242, 702
—, detection in ethylene, 1259, 1260
—, — butadiene, 701
—, — liquid air, 702
—, — nitrogen, 701
—, diethyl carbonate solvent for, 169
—, diethyl oxalate solvent for, 169
—, entropy of formation, 1282-1284
—, estimation of, 1124, 1144, 1145
—, ethylene from, 719
—, explosive nature of, 701
—, extraction from gas mixtures, 169, 171, 701
—, formic acid from, 904
—, free energy of formation, 1282-1284
—, —, effect of temperature, 1294
—, from benzene, 95, 259
—, from butane, 64, 166, 168
—, from 1-butene, 83
—, from calcium carbide, 701
—, from coke oven gas, 170
—, from cracking operations, 131, 140
—, from ethane, 56
—, from ethylene, 57, 79, 160, 166, 168
—, from ethylene dibromide, 505
—, from ethylene dichloride, 497
—, from free radicals, 53, 75
—, from isobutane, 66, 67, 166
—, from isobutene, 84
—, from kerosene, 253
—, from methane, 54, 55, 165, 166, 168, 218, 254, 257, 892
—, from natural gas, 168
—, from olefins, 255
—, from petroleum hydrocarbons, 253, 254
—, from propane, 61, 166, 169, 187, 254
—, from propene, 81, 187
—, from tars, 254
—, from toluene, 260
—, gasoline from, 704
—, heat of formation, 1282-1284
—, heavy, reaction with chlorine, 742, 743
—, hydration of, 712, 713, 714
—, hydrogenation of, 171, 704, 719
—, ignition temperature of, 988
—, inflammability limits of, 980
—, in motor fuels, 701, 1039, 1040
—, mechanism for oxidation of, 902, 903
—, mechanism for ozonization of, 904
—, methenyl radical from, 89
—, molal entropy of, 1282, 1283, 1284
—, nascent, polymerization of, 187
—, oxalic acid from, 904
—, oxidation of, 849, 850, 902, 904
—, peroxides from, 924
—, phosphine removed from, 170
—, photobromination of, 711
—, photochemical decomposition of, 264, 265
—, polymerization of, 57, 89, 264-267, 680, 702-704
—, properties of, 701
—, pyrolysis of, 88, 89, 703
—, reaction with acetaldehyde, 680
—, — acetic acid, 717
—, — alcohols, 714
—, — alkyl mercury bromides, 724
—, — amines, 719
—, — ammonia, 719
—, — aniline, 719
—, — benzene, 718
—, — chlorine, 709
—, — cresols, 715
—, — dichloromethylarsine, 721
—, — ethylacetoacetate, 721
—, — ethylbenzene, 719
—, — hydrogen chloride, 716
—, — hydrogen fluoride, 716
—, — hydrogen sulphide, 720
—, — iodine, 711
—, — mercaptans, 472, 473, 715
—, — mercury salts, 702
—, — β-naphthol, 715
—, — organic acids, 717
—, — ozone, 904
—, — phenol, 715
—, — selenium, 720
Acetylene, reaction with sodium hypoiodide, 711
—, — sulphur, 467, 485, 720
—, — thiocresol, 473
—, — toluene, 718
—, removal of acetone from, 1264
—, removal of hydrogen sulphide from, 170
—, storing of, 171, 701
—, thiophene from, 467
—, thiophenol from, 467
—, toxicity of, 1264
—, use of calcium chloride in purification of, 170
—, — chlorine in preparation of, 168
—, — hydrogen in preparation of, 168
—, — hydrogen chloride in preparation of, 168
—, — lime in purification of, 170
—, uses of, 701
—, γ-valero-lactone solvent for, 169
—, vinylacetylene from, 704
—, vinyl resins from, 253
Acetylene addition, mechanism for mercury catalysis in, 722
Acetylene black, ash content of, 244
—, benzene in, 244
—, carbon tetrachloride vapor adsorbed by, 252
—, in dry cells, 251
—, in liquid oxygen explosives, 251
—, iron in, 244
—, naphthalene in, 244
—, phenanthrene in, 244
—, preparafion of, 223, 242
—, properties of, 244
—, removal of iron from, 244
—, silica in, 244
Acetylene carboxylic acids, preparation of, 829
Acetylene diiodide, formation of, 711
Acetylene-ethane, azeotropic mixture of, 30, 1140
Acetylene homologues, effect of lead tetraethyl on, 1019, 1020
Acetylene hydrocarbons, refining with, 719
Acetylene-hydrogen mixtures, chlorination of, 709
Acetylenes, from amylene dibromide, 513
Acetylene tetrachloride, dechlorination of, 710
—, formation of, 709
—, in cleaning compositions, 732
Acetylenic alcohols, preparation of, 724
Acetylenic Grignard reagents, preparation of, 724
Acetyl iodide, reaction with cyclohexene, 611
—, — divinyl ether, 612
—, — furan, 612
—, — thiophene, 611
Acetylketene, heat of formation, 442
Acetylmandelic acetic anhydride, preparation of, 439
2-Acetyl-3-methylbutane, preparation of, 1099
2-Acetyl-1-methylcyclopentane, formation of, 205
2-Acetylpentane, preparation of, 444, 1099
Acetylphthalimide, acetone from, 423
Acetylsalicylic acetic anhydride, preparation of, 439
Acid anhydrides, condensation with conjugated diolefins, 687, 688, 689, 690
—, from ethylene glycol esters, 540
—, from paraffin wax, 971
—, reaction with aldehydes, 885
Acidation, of oil wells, 9
Acid halides, reaction with olefins, 609-614
Acidic oxides, catalysts, reaction of olefins and carbon monoxide, 625, 626
Acidity, determination of, 1166, 1167
Acidosis, effect of ethylene on, 1260, 1261
Acids, aliphatic, sulphates from, 1086
—, as demulsifying agents, 969, 1075
—, by aquolysis, 131
—, by oxidation of petroleum, 962, 964-966
—, catalyst, ethylene oxide-hydrogen sulphide reaction, 564
—, —, polymerization of aldehydes, 886
—, condensation with conjugated diolefins, 688, 690, 691
—, decolorizing with clay, 976, 977
—, effect on stability of naphthenes, 937
—, esterification of, 314

Acids, formation in gasoline, 922
—, from alcohols, 1050, 1052
—, from butane, 874
—, from carbon monoxide and hydrogen, 1223, 1244, 1245
—, from cyanohydrins, 886
—, from ethane, 871, 872
—, from gasoline, 861
—, from Kogasin, 1255
—, from methane and steam, 870
—, from 2-methylpropene, 622
—, from mineral oil, 856
—, from naphtha, 881
—, from olefins and carbon monoxide, 625
—, from oxidation of olefins, 553
—, from oxidation of transformer oil, 935
—, from paraffin wax, 843, 865, 1255
—, from pentane, 859
—, from petroleum ether, 854
—, from propane, 862, 863
—, from still vapors, 1047
—, gasoline-soluble, from ceresins, 975
—, in co-polymerization of chloroprene, 681, 682
—, in gasoline, 908
—, in gum formation, 921
—, in pressure distillates, 1104
—, oxidation of, 852
—, plastics from, 969
—, removal of, from gasoline, 1047
—, separation by acetic acid, 977
—, — alkali bases, 976
—, — alkali carbonate, 975
—, — ammonia, 976, 977
—, — benzene, 967, 968
—, — benzine, 967, 968, 975
—, — calcium hydroxide, 976
—, — calcium hypochlorite, 968
—, — fractional crystallization, 959
—, — fractional distillation, 958, 960, 977
—, — gasoline, 976
—, — hydrogenation, 975, 976
—, — isopropyl alcohol, 975
—, — lime, 967
—, — methyl alcohol, 975, 977
—, — oxidation, 960
—, — phosphoric acids, 977
—, — pyridine, 977
—, — sulphur dioxide, 967, 977
—, — trichloroethylene, 967, 968
—, treatment of gasoline with, 927
—, use in lubricants, 968
—, — rubber vulcanization, 969
—, wetting agents from, 1076
Acid sludge, hydrolysis of, 486
—, reaction with olefins, 669
Acrolein, for solvent extraction, 43
—, from dibromocyclopropane, 762
—, from glycerol, 878
Acrylic acid, from ethylene chlorohydrin, 527
Acrylic acid esters, polymers of, 527
Acrylonitrile, reaction with monoethanolamine, 569
Actinic light, action on motor fuels, 268
—, effect on color stability of fuels, 926
—, use in amylene chlorination, 511
—, — butane chlorination, 752
—, — butene di-iodide synthesis, 511
Actinic rays, use in propane chlorination, 750
Activated aluminum silicate, use in cracking, 128
Activated carbon, catalyst, acetone from acetic acid, 423
—, —, esterification of ethylene glycol, 540
—, —, polymerization of olefins, 171
—, —, pyrolysis of methane, 169
—, use in clarifying wines, 232
Activated charcoal, catalyst, reaction of monovinylacetylene and hydrogen chloride, 680
—, —, esterification of propene, 307
—, —, trimethylacetic acid from acetone, 432
Activated fuller's earth, use in progressive catalysis, 114
Activation energies, for free radicals from hydrocarbons, 51
Activation-energy, of hydrogen halides, 301
—, of triphenylmethyl chloride, 826
Activity, definition of, 1296
Acylaminophenols, antioxidants for gasoline, 916
Acyl urea, stabilization of carbon tetrachloride, 730, 731
Adamantane, isolation from crude oil, 35
Adhesion energies, of asphalts, 1213
Adiabatic transformation, definition of, 1335
Adipic acid, alkoxyalkyl esters, as plasticizers, 544
—, from cyclohexanone, 450
—, from cyclohexene, 895
—, from nitrocylohexane, 1093
Adipic anhydride, antioxidant for transformer oil, 941
Adsorbent carbon, production of, 227
Adsorbent clays, desulphurizing agents, 489
Adsorbent silicates, use in cracking, 129
Adsorbents, use of in refining, 31
Adsorption, of hydrocarbons by silica gel, 31
Adsorption agent, fuller's earth as, 1109
Adsorption agent, gumbrin as, 1109
Adsorptive catalysts, in refining of gasoline, 135
Aerobacter, in fermentation of sucrose, 547
Aerogel, definition of, 446
Aetox gas, definition of, 556
Agar agar, in asphalt emulsions, 1219
Air, absorption by mineral oil, 939
—, effect on hydrogen bromide-allyl bromide reaction, 315
—, — hydrogen bromide-undecenoic acid reaction, 318
—, — hydrogen bromide-vinyl bromide reaction, 315
—, — polymerization of olefins, 661, 672
—, — voltolization, 261
—, ozonized, use in drying oil preparation, 1054
Albuminous substances, in crude oil, 12
Alcoholates, reaction with alkyl halides, 825
—, — aralkyl halides, 825
Alcohol-benzol-gasoline blends, as motor fuels, 1038
Alcohol-gasoline blends, as motor fuels, 1034-1039
—, octane number of, 1251
Alcohols, acetylation by ketene, 438
—, acids from, 1052
—, action of electric discharges on, 262
—, aldehydes from, 399, 844
—, as blending agents, 1035
—, as extraction agents, 972
—, as plasticizing agents, 1112
—, butadiene from, 676, 677
—, by aquolysis, 131
—, by reduction of carbon monoxide, 1049, 1223, 1244, 1251, 1252, 1303-1305
—, combustion of, 999
—, condensation of, 341
—, — with phenols, 402, 403
—, conversion to higher alcohols, 341
—, cyclopentadiene from, 676
—, decomposition of, catalyst for, 155
—, decrease of induction period by, 909
—, dehydration of, 394, 399, 406, 558, 1051, 1052
—, drying agents for, 407
—, esterification of, 1080, 1081, 1118-1120
—, estimation, in blended fuels, 1185
—, ethers from, 406, 579
—, extractants for asphalts, 1202
—, formals from, 889
—, free energy of formation, 1294, 1295
—, from aldehydes, 885, 886, 889
—, from butane, 859, 874
—, from cracking gases, 146
—, from ethane, 857, 858, 871, 872
—, from Gasol, 1255
—, from gasoline, 861
—, from heptane, 859, 865
—, from methane and steam, 870
—, from mineral oil, 856
—, from naphtha oxidation, 876
—, from natural gas, 23
—, from oxidation of asphalt, 1203
—, — hydrocarbons, 865
—, — olefins, 893

Alcohols, from oxidation of petroleum, 843, 962, 963, 964, 965
—, from oxygenated paraffins, 340
—, from paraffin wax, 865, 971, 1056
—, from pentyl chloride, 755
—, from petroleum ether, 854
—, from photochemical decomposition of acetone, 450
—, from propane, 858, 862, 863
—, from residual oils, 1050
—, from terpenes, 624
—, halogenated, preparation of, 522, 523, 524
—, —, uses of, 523
—, in cleaning agents, 1084
—, in insecticides, 1078
—, in vulcanization of rubber, 1078
—, ketones from, 399, 421
—, olefins from, 155, 420
—, oxidation of, 399, 420, 423, 844, 849, 877-880, 931
—, polyhydric, desulphurizing agents, 488
—, —, *see* Polyhydric alcohols
—, precipitation of asphalt by, 935
—, pyrolysis of, 155, 213
—, reaction with acetylene, 714
—, — alkylacetylenes, 723
—, — benzene, 402
—, — carbon monoxide, 1041, 1050
—, — ethers, 715
—, — ethylene oxide, 548
—, — formaldehyde, 889
—, — isobutene oxide, 589
—, — vinylactylene, 705
—, — wax acids, 975
—, removal from ether, 336
—, solubility in water, 404
—, stabilization of soap suspensions by, 409
—, sulphation of, 1085
—, wetting agents from, 1076
Aldehyde-acids, from petroleum distillates, 843, 863, 864, 1053
Aldehyde-alcohols, from petroleum distillates, 843, 1053
Aldehyde-hydroxy acids, from petroleum distillates, 843, 1053
Aldehydes, alcohols from, 885, 886, 889
—, aldoximes from, 886
—, applications of, 889-891
—, as antiknocks, 1018
—, carboxylic acids from, 885
—, condensation of, 886
—, condensed with ketones, 443
—, cyanohydrins from, 886
—, cyclic acetals from, 544
—, decomposition of, 883, 884
—, detection in ethylene, 1259
—, diethers from, 889
—, effect on stability of naphthenes, 937
—, esters from, 889
—, formals from, 889
—, formation in gasoline, 922
—, from alcohols, 331, 399, 844, 1052
—, from aquolysis, 131
—, from asphalt oxidation, 1203
—, from butane, 874
—, from 2,3-butene glycol, 536
—, from carbon monoxide and hydrogen, 1223, 1244
—, from ethane, 857, 858, 871, 872
—, from ethylene glycol, 536
—, from gas oil, 864
—, from gasoline, 861
—, from hexane, 1014
—, from methane and steam, 870
—, from naphtha oxidation, 875, 876, 881
—, from oxidation of olefins, 553
—, — petroleum, 962, 964-966, 1053, 1056
—, from paraffin wax, 865, 971
—, from petroleum distillates, 843
—, from petroleum ether, 853, 854
—, from propane, 858, 862, 863
—, from residual oils, 1050
—, from still vapors, 1047
—, from wax acids, 979
Aldehydes, in co-polymerization of chloroprene, 681, 682
—, in gasoline, 908
—, in gum formation, 921
—, in perfumery, 875, 881
—, in pickling solutions, 890
—, in refining, 625
—, nitriles from, 886
—, nitro alcohols from, 888
—, nitro-glycols from, 888
—, oxidation of, 885, 931
—, polymerization of, 886, 889, 890
—, products with nitric acid, use of, 851, 852
—, pyridine bases from, 885, 886
—, reaction with acid anhydrides, 885
—, — ammonia, 885
—, — ammoniacal silver, 885
—, — ammonium cyanide, 886
—, — glycols, 582, 889
—, — Grignard reagents, 886
—, — hydrazine, 886
—, — hydrogen cyanide, 886
—, — hydroxylamine, 886
—, — mercaptans, 473, 474
—, — nitro compounds, 888, 1095
—, — olefins, 623
—, — sulphonic acids, 1081
—, recovery of, 884, 885
—, reduction of, 885, 889
—, removal from ether, 336
—, — gasoline, 1047
—, resins from, 625, 886, 1081
Aldol-α-naphthylamine, antioxidant for gasoline, 918
Aldoximes, from aldehydes, 886
Aliphatic compounds, in crude oil fractions, 13
Aliphatic halides, reaction with sulphites, 819
—, sulphonic acids from, 819, 820
Aliphatic hydrocarbons, conversion to acetylene, 168
—, crystalline, preparation of, 31
—, cyclization of, 73
—, olefins from, 160
Aliphatics, effect on knock rating, 1024, 1025
—, from carbon monoxide and hydrogen, 1235
—, estimation in benzene, 1150
—, oxygenated, free energy relations of, 1286
—, reaction with sulphuric acid, 1082
Aliphatic sulphonic acids, as refining agents, 930
Alkadienes, bromination of, 1152
—, estimation of, 1152
Alkali, activation by mahogany sulphonates, 1077
—, as extraction agent, 976, 1104, 1105
—, catalyst, condensation of acetaldehyde, 889
Alkali alkoxides, as dehydrating agents, 330
—, catalysts, reaction of olefins and carbon monoxide, 626
Alkali carbonates, catalyst, oxidation of petroleum, 964
—, —, reaction of olefins and carbon monoxide, 626
—, for separation of acids, 975
—, — sulphonic acids, 1071
—, for sulphur removal, 1249
Alkalies, catalysts, polymerization of aldehydes, 886
—, emulsifying agents for asphalts, 1217
Alkali fatty acid salts, catalysts, reaction of olefins and carbon monoxide, 626
Alkali halides, catalysts, reaction of olefins and carbon monoxide, 625
Alkali hydroxides, catalysts, reaction of olefins and carbon monoxide, 626
—, reaction with ethyl alcohol, 342
—, — olefins, 629
Alkali metal caseinate, stabilization of asphalt emulsions with, 1218
Alkali metals, in refining of gasoline, 929
—, reaction with diolefins and amines, 698
—, — ethyl alcohol, 342
Alkaline-earth alkoxides, catalysts, reaction of olefins and carbon monoxide, 626

Alkaline-earth carbonates, catalysts, methane oxidation, 264
—, —, oxidation of petroleum, 964
—, —, reaction of olefins and carbon monoxide, 626
Alkaline-earth fatty acid salts, catalysts, reaction of olefins and carbon monoxide, 626
Alkaline-earth hydrides, in refining of gasoline, 929
Alkaline-earth hydroxides, catalysts, reaction of olefins and carbon monoxide, 626
—, —, reaction of sulphur and hydrocarbons, 467
Alkaline-earth metal halides, catalysts, reaction of olefins and carbon monoxide, 625
Alkaline-earth metal salts, promoters, oxidation of anthracene, 952
Alkaline-earth oxides, catalysts, methane oxidation, 264
—, —, oxidation of petroleum, 964
—, —, reaction of sulphur and hydrocarbons, 467
Alkaline-earth phosphates, catalyst, hydration of ethylene, 287
Alkali phenoxides, dehydrating agents, 330
Alkali phosphates, catalyst, methane-carbon dioxide reaction, 870
—, in cleaning agents, 1112
Alkali rosinates, in asphalt emulsion preparation, 1217
Alkali salts, promoters, oxidation of anthracene, 952
Alkali sludge, asphaltenes in, 1105
—, naphthenic acids in, 1105
—, resins in, 1105
Alkaloids, preparation of, 688
Alkanes, as anesthetics, 1256
Alkene glycols, reaction with phthalic acid, 542
Alkenes, from secondary alcohols, 400
—, *see* Olefins
Alkoxyalkyl halides, reaction with butadiene, 698
Alkoxy chlorides, *see* Alkyl hypochlorites
2-Alkoxy-2-trichloromethyl-1,3-dioxolanes, properties of, 541
Alkylacetylenes, formation of, 721, 722
—, Grignard reagents from, 724
—, reaction with acetic acid, 722
—, — acetyl chloride, 724
—, — alcohols, 722, 723
ter-Alkyl adipic acids, formation of, 605
Alkylamines, preparation of, 804, 808
Alkylaryl ketones, in motor fuel, 1039
Alkylated naphthalenes, voltolization of, 262
Alkylated phenols, uses of, 604, 605, 916
Alkylated polyphenols, antioxidants for gasoline, 916
Alkylation, of anthracene, 595, 596
—, of gasoline, 593
—, of naphthenes, 594, 601, 602, 603
ter-Alkyl benzenes, oxidation of, 942, 943
Alkyl chlorosulphites, preparation of, 413
Alkyl compounds, as antiknocks, 1017
Alkyl cyanamides, for stabilizing carbon tetrachloride, 730
Alkylene diamines, antioxidants for white oils, 937
Alkyl esters, recovery of, 305
Alkyl ethers, catalysts, oxidation of paraffins, 874
ter-Alkyl ethers, preparation of, 544, 606, 607
Alkyl gallates, antioxidants for gasoline, 917
Alkyl halides, alkylation of aromatics with, 811
—, catalysts, carbon monoxide-methyl alcohol reaction, 1050
—, decomposition of, 805
—, ethers from, 804
—, olefins from, 804
—, polymerization of, 811
—, reaction with alcoholates, 825, 826
—, — amines, 804, 808
—, — ammonia, 804, 808
—, — hydrocarbons, 804
—, — magnesium, 804, 822
—, — mercaptans, 479
—, — metallic cyanides, 822
—, — sodium sulphide, 479
—, — thiosulphates, 829
Alkyl halides, sulphonates from, 804
—, sulphur plastics from, 828
Alkyl hypochlorites, reaction with olefins, 626, 627
Alkyl hypohalites, preparation of, 346
Alkylidene diesters, preparation of, 717
Alkylmagnesium iodides, reaction with nitroparaffins, 1096
Alkyl mercury bromides, reaction with acetylene, 724
N-Alkyl morpholines, preparation of, 583
Alkyl nitrates, as ignition promoters, 1096
Alkyl nitrites, as ignition promoters, 1097
Alkylolamines, corrosion inhibitors, 577
—, heat-resistant agents, 577
—, naphthenic sulphonic salts of, 575
—, phosphorized esters, rust preventives, 576
—, recovery of, 577
Alkylolamine soaps, in hydraulic cement, 575
Alkyl oxalates, as antiknocks, 1017
p-ter-Alkylphenols, preparation of, 402
Alkyl phthalates, as antiknocks, 1017
Alkyl resorcinol, preparation of, 813
Alkyl sulphates, hydrolysis of, 325, 394-397
—, reaction with acetates, 396, 397
Alkyl sulphides, estimation of, 1159
Alkyl sulphonic acids, decomposition of, 1067, 1068
—, from mercaptans, 1066
—, hydrolysis of, 1067, 1068
—, stability of, 1067, 1068
Alkyl sulphur chlorides, disulphides from, 478
—, reaction with cyanides, 478
—, — stannites, 478
—, — sulphites, 478
Alkyl sulphuric acids, reaction with mercaptans, 472
Alkyne peroxides, oxidizing properties of, 903
Alkynes, oxidation of, 903, 904
Allene, from petroleum hydrocarbons, 255
—, — propene, 75
—, — propene dichloride, 508
—, nitrosite from, 696, 697
—, reaction with nitrogen trioxide, 696, 697
Allowable boost ratio, definition of, 1027
Alloys, catalytic action on decomposition of olefins, 77
—, mechanical stability of, 134
—, resistance to corrosion, 134
—, resistance to oxidation, 134
Alloy steel, in cracking unit construction, 133, 150
Allyl acetic acid, reaction with hydrogen bromide, 318
Allyl alcohol, from propene oxide, 586
—, glycerol from, 895
Allylamine, as antiknock, 1018
Allyl bromide, reaction with hydrogen bromide, 315
Allylcyclohexane, pyrolysis of, 93, 94
Allylene, from petroleum hydrocarbons, 255
Allyl ethers, reaction with sulphur dioxide, 616
Allyltoluene, pyrolysis of, 96
Alpha bonds, thermal stability of, 96
Alpha particles, action on acetylene, 267
Alum, reaction with diethyl pinacone, 678
Alumel catalyst, pyrolysis of olefins, 77
Alumina, catalyst, alkylation of phenols, 605
—, —, cracking of petroleum, 111, 128
—, —, cyclization of paraffins, 74, 190
—, —, dehydration of alcohol, 331, 399, 400
—, —, — ethylene glycol monoethylether, 174
—, —, — Synthol, 1252
—, —, dehydrogenation of cyclohexane, 93
—, —, — paraffins, 159
—, —, esterification of propene, 307
—, —, ether from ethyl alcohol, 331, 332
—, —, ethyl alcohol from ether, 332, 333
—, —, ethylation of amines, 346
—, —, ethylene oxide-hydrogen sulphide reaction, 564
—, —, hydration of ethylene, 288-291
—, —, hydrogenation of acetylene, 171
—, —, — propene oxide, 586
—, —, ketone-alcohol reaction, 443

Alumina, catalyst, methane-steam reaction, 273-276, 278
—, —, polymerization of ethylene oxide, 562
—, —, — olefins, 643, 1042
—, —, preparation of allyl alcohol, 586
—, —, — unsaturated ketones, 444
—, —, pyrolysis of alcohols, 155, 173
—, —, — cyclobutane, 89
—, —, — cyclopropane, 89
—, —, — methane, 169, 223
—, —, — oxygenated hydrocarbons, 340
—, —, reaction of benzal chloride and dimethyl ether, 794
—, —, — chloroform and dimethyl ether, 729
—, —, — *m*-cresol and ammonia, 788
—, —, — ethers and alkyl halides, 345
—, promoter, activated fuller's earth, 114
—, —, in reforming, 280
—, —, methane-carbon dioxide reaction, 274
—, —, reduction of carbon monoxide, 1228, 1234, 1236, 1239, 1240
Alumina gel, catalyst, isomerization of propene oxide, 586
—, —, esterification of propene, 307
Alumina-phosphoric acid, catalyst, dehydrogenation of cyclohexane, 93
Alumina-zinc chloride, catalyst, dehydrogenation of cyclohexane, 93
Aluminum, activated by mercuric chloride, 813
—, aluminum chloride from, 204
—, amalgamation of, 197
—, catalyst, acetone-ethanol reaction, 443
—, —, cyclization of paraffins, 189
—, —, decomposition of methane, 257
—, —, desulphurization of gasoline, 490
—, —, diphenylene oxide-chlorinated paraffin reaction, 758
—, —, of halogenation, 490
—, —, in cracking, 114, 813
—, —, oxidation of kerosene, 965
—, —, — methane, 869
—, —, — naphthalene, 946
—, —, — paraffins, 874
—, —, polymerization of olefins, 665
—, —, pyrolysis of acetals, 715
—, —, — ethylene, 172
—, —, — methane, 180
—, estimation of sulphur with, 1162
—, inhibitor, deterioration of ethylene oxide, 554
—, promoter, oxidation of methyl alcohol, 878
—, —, reaction of aldehydes and cracked distillates, 625
—, —, — nitrosyl chloride and hydrocarbons, 112
—, —, reduction of carbon monoxide, 1229, 1230, 1231, 1240, 1242, 1248
—, reaction with alcohols, 342, 343
—, refining gasoline with, 668
—, refining isopropyl alcohol with, 365
Aluminum alkoxide, preparation of, 342, 372
—, action on aldehydes, 372
Aluminum amalgam, reducing agent, 547
Aluminum antimonides, catalysts, dehydrogenation of alcohols, 419
Aluminum arsenides, catalysts, dehydrogenation of alcohols, 419
Aluminum behenate, in mineral oil, 543
Aluminum bismuthates, catalysts, dehydrogenation of alcohols, 419
Aluminum bromide, action on benzene, 207
—, — pentane, 201
—, catalyst, bromination of cyclohexane, 769
—, —, — toluene, 795
—, —, esterification of ethylene, 304
—, —, — propene, 308, 316
—, —, halogenation of naphthenes, 760
—, —, polymerization of olefins, 665
—, —, phosgene-*n*-pentane reaction, 446
Aluminum carbonate, catalyst, oxidation of methane, 881
Aluminum chloride, action on alkylbenzenes, 208
—, — aromatics, 206-208
—, — chlorinated Kogasin, 814, 1253, 1254
—, — cycloolefins, 204, 645
—, — cracked gasoline, 209, 212, 216, 263, 927, 929
Aluminum chloride, action on cracked mineral oil, 216
—, — *sec*-butylphenyl ether, 403
—, — Kogasin, 1253, 1254
—, — naphthenes, 196, 204-206, 211
—, — olefins, 202-204, 209, 210, 255, 635, 643, 665, 671, 674, 675
—, — paraffins, 198-201
—, — petroleum stocks, 215
—, — pyrene, 215
—, catalyst, acetylene-dichloromethylarsine reaction, 721
—, —, alkylation of acid halides, 609, 611, 612
—, —, — aromatics, 382, 383, 401-403, 411, 412, 418, 592, 595, 596, 815
—, —, — alcohols, 606
—, —, — naphthenes, 601
—, —, — paraffins, 599, 602
—, —, — phenols, 416, 605, 606
—, —, — phenyl ethers, 606
—, —, benzene-ethylene chloride reaction, 815
—, —, benzine-acetyl chloride reaction, 1099
—, —, benzoyl chloride-benzene reaction, 815
—, —, bromination of benzene, 790, 791
—, —, chlorination of ethylene, 494
—, —, condensation of alkyl halides, 811
—, —, — chloroform and *p*-dichlorobenzene, 729
—, —, — fluorotrichloromethane, 737
—, —, — *ter*-alkyl hypohalites and phenols, 418
—, —, co-polymerization of olefin and diolefin, 216
—, —, dichloroethane-vinyl chloride reaction 811
—, —, esterification of olefins, 300-303, 306, 308, 310
—, —, ether from ethyl alcohol, 331
—, —, ether-hydrogen chloride reaction, 345
—, —, ethyl alcohol from ether, 333
—, —, ethylene oxide-benzene reaction, 563
—, —, ethylene oxide-hydrogen sulphide reaction, 564
—, —, hydrogenation of stilbene, 207
—, —, isomerization of cyclohexane, 1302
—, —, naphthalene-chlorinated wax reaction, 817
—, —, paraffin-carbon monoxide reaction, 1099
—, —, paraffin-ethylene oxide reaction, 1101
—, —, paraffin-phthalic anhydride reaction, 1101
—, —, phosgene-paraffin reaction, 1101
—, —, polymerization of slack wax, 212
—, —, — sweater oil distillate, 212
—, —, production of lubricants, 211, 213, 214, 758
—, —, reaction of acetyl chloride and naphthalene, 447
—, —, — acetyl chloride and paraffins, 444, 1099
—, —, — amyl chloride and gas oil, 812
—, —, — benzene and acetylene, 718
—, —, — benzene and carbon monoxide, 949, 957
—, —, — benzene and ketene, 439
—, —, — benzene and sulphur, 468
—, —, — benzene and *n*-tridecane, 1254
—, —, — chlorinated Kogasin and aromatics, 1253, 1254
—, —, — chlorobenzene and acetic anhydride, 789
—, —, — chloro-*n*-tetradecane and xylene 1254
—, —, — hydrogen chloride and butadiene compounds, 686
—, —, — olefins and acid chlorides, 613
—, —, — olefins and chloroesters, 614
—, —, — petrolatum and carbon tetrachloride, 732
—, —, — phthalide and chlorobenzene, 789
—, —, — toluene and acetic anhydride, 448
—, —, voltolization, 262
—, cracking with, 112, 195, 197, 198
—, decolorization of asphalts with, 1192
—, desulphurizing agent, 434, 488
—, double compounds with olefins, 215
—, effect on exchange reaction between hydrogen and deuterium, 206, 207
—, hydrogenation action of, 198
—, promoter, hydration of propene, 291
—, purification of phthalic anhydride, 961
—, reaction with alcohols, 383

Aluminum chloride, reactivation by nitrosyl chloride, 198
—, —, trichloromethane-dichloroethylene reaction, 811
—, —, vinyl chloride-hydrogen chloride reaction, 716
Aluminum chloride sludge, unsaturated oil from, 201
Aluminum coating, for steels, 134
Aluminum compounds, catalysts, chlorination of benzene, 778
—, —, reaction of olefins and alkali hydroxides, 629
Aluminum ethoxide, preparation of, 342, 343
Aluminum fluoride, catalyst, preparation of propyl fluoride, 307
Aluminum halides, catalyst, halogenation of cyclopropane, 761
Aluminum hydrosilicate, catalyst, dimerization of ethylene oxide, 579
—, use in cracking, 115
Aluminum hydroxide, in decomposition of methane, 227
—, in methane-steam reaction, 278
—, reaction with ethylene oxide, 560
Aluminum iodide, in phosgene-*n*-pentane reaction, 446
Aluminum isopropoxide, preparation of, 372
—, in reduction of aldehydes, 889
Aluminum naphthenates, antioxidants for lubricants, 937
—, in insecticides, 1115
—, in lubricants, 1116
Aluminum nitrate, effect on ignition temperature, 986, 987
—, in methane-steam reaction, 278
—, reaction with 2,7-dimethyloctane, 1090
Aluminum oleate, in asphalt emulsion preparation, 1216
Aluminum oxide, catalyst, chlorination of toluene, 793
—, —, decarboxylation of phthalic anhydride, 950, 951
—, —, dechlorination of propyl chloride, 805
—, —, decomposition of ether, 334
—, —, dehydrogenation of alcohol, 337
—, —, dehydrogenation of dimethylcyclohexane, 185
—, —, ethyl alcohol from ether, 334
—, —, hydrogen-carbon monoxide reaction, 661
—, —, hydrolysis of chlorobenzene, 782, 783
—, —, hydrolysis of methyl chloride, 796
—, aluminum sulphate from, 364
—, catalyst, chlorination of acetylene, 743
—, —, — propane, 750
—, —, condensation of acetone, 431
—, —, dehydration of glycols, 548
—, —, dehydrogenation of isopropanol, 421
—, —, esterification of isobutene, 752
—, —, hydration of acetylene, 712
—, —, — mesityl oxide, 423
—, —, methane-steam reaction, 278, 270
—, —, nitric oxide-paraffin reaction, 1091
—, —, oxidation of aromatics, 942, 946
—, —, — furfuraldehyde, 945
—, —, — hydrocarbons, 850, 851
—, —, — methane, 881
—, —, polymerization of ethylene, 637
—, —, — 2-pentene, 643
—, —, pyrolysis of benzene, 192
—, —, — butene dichloride, 510
—, —, — isobutyl bromide, 806
—, —, — thiophene, 483
—, —, reaction of amines and alcohols, 614
—, —, — furan and hydrogen sulphide, 463
—, —, — methanol and carbon monoxide, 1050
—, —, reduction of carbon monoxide, 1048
—, —, reforming of gasoline, 189
—, effect on ignition temperature, 1000
Aluminum palmitate, catalyst, oxidation of petroleum, 964
—, use in mineral oil, 543
Aluminum phosphate, catalyst, alkylation of phenols, 605
—, —, esterification of propene, 308
—, —, hydration of ethylene, 287, 290
—, —, oxidation of ethane, 872
—, —, — methane, 869
—, —, pyrolysis of olefins, 190
—, —, reaction of ethers and alkyl halides, 345
Aluminum phosphides, catalysts, dehydrogenation of alcohols, 419
Aluminum salts, catalyst, acids from alcohols, 1051
Aluminum selenides, catalysts, dehydrogenation of alcohols, 419
Aluminum silicate, catalyst, alkylation of phenols, 605
—, —, hydration of ethylene, 288
—, —, in cracking operations, 128, 137
—, —, pyrolysis of benzene, 192
Aluminum soaps, as driers, 1055
—, catalysts, oxidation of paraffin wax, 972
Aluminum stearate, as pour point depressant, 577
—, catalyst, oxidation of petroleum, 964
—, in anti-rust compositions, 577
—, in mineral oil, 543
Aluminum sulphate, as antioxidant, 914
—, by-product, hydrolysis of isopropyl sulphates, 364
—, catalyst, esterification of propene, 308
—, —, ether from ethyl alcohol, 331
—, —, hydration of ethylene, 283, 289, 290
—, in insecticides, 1112
Aluminum sulphide, desulphurizing agent, 489
Aluminum sulphonate, properties of, 1067
Aluminum tellurides, catalysts, dehydrogenation of alcohols, 419
Aluminum vanadate, catalyst, decarboxylation of esters, 952
—, —, phthalic anhydride-carbon monoxide reaction, 950
Alundum, use in pyrolysis, 167
Amine-olefin method, for structure of naphthenic acids, 1104, 1111
Amines, addition to cracked distillates, 135
—, as antioxidants, 915, 927
—, catalysts, condensation of sulphonic acids and aldehydes, 1081
—, —, polymerization of aldehydes, 889
—, —, — olefins, 672
—, color stabilizers, 926
—, cracking of, 158
—, critical oxidation potential of, 920
—, emulsifying agents from, 891
—, extraction agents, 44, 976
—, for hydrogen sulphide removal, 458
—, for refining alcohols, 408
—, from acetone, 428
—, from ammonia and olefins, 281
—, from chlorohydrins, 524
—, from nitrocycloparaffins, 1095
—, inhibitors, polymerization of chloroprene, 681
—, —, tetralin autoxidation, 906
—, reaction with acetone, 428
—, — alkyl halides, 808
—, — cyclohexanol, 614
—, — diolefins, 698
—, — ethyl alcohol, 346, 347
—, — ethylene chlorohydrin, 527
—, — olefins, 614, 615
Amino acids, from nitriles, 886
—, inhibitors, gum formation, 915
Aminoazobenzenes, antioxidants, 917
p-Aminobenzoates, local anesthetic, 1256
p-Aminobiphenyl, preparation of, 787
Aminochrysenes, antioxidants, 918
Amino-diaryl ethers, antioxidants, 938
N-Aminodiethylethanol, reaction with 8-amino-6-methoxyquinoline, 569
—, — α-aminopyridine, 569
—, — aniline, 569
—, — 6-chloro-8-amino-quinoline, 569
N-Aminodiethylpropanol, reaction with 8-amino-6-methoxyquinoline, 569
Amino groups, gum inhibitors, 914
Amino-hydroxy-phenones, antioxidants, 916

5-Amino-2-hydroxytoluene, antioxidant, 916
8-Amino-6-methoxyquinoline, reaction with N-amino-diethylethanol, 569
Aminophenanthrenes, antioxidants, 918
Aminophenols, antioxidants, 916
Amino-phenones, antioxidants, 916
β-*p*-Aminophenylaminoethyl alcohol, preparation of, 560
Aminopicenes, antioxidants, 918
α-Aminopyridine, reaction with N-aminodiethylethanol, 569
8-Amino-1,4,5-trihydroxy naphthalene, antioxidant, 916
Ammonia, affinity for olefins, 162
—, catalyst, condensation of phenols and aldehydes, 890
—, —, polymerization of dichlorobutenes, 685
—, color stabilizer for fuels, 926
—, desulphurizing agent, 489
—, effect on Kogasin synthesis, 1236
—, estimation in gases, 1127
—, for fractionation of olefins, 162
—, for hydrogen sulphide removal, 459
—, for hydrolysis of alkyl sulphates, 394, 396
—, for separation of acids, 976, 977
—, from decomposition of ethanolamines, 570
—, from nitric oxide-paraffin reaction, 1091
—, ignition temperature of, 987
—, in asphalt manufacture, 1206
—, in preparation of resins, 216
—, in refining of sulphonates, 1072, 1073
—, inflammability limits of, 980
—, liquefied, for absorption of acetylene, 169
—, pressure-volume-temperature relations, 1321, 1322
—, reaction with acetone, 428
—, — acetylene, 719
—, — aldehydes, 885
—, — alkyl halides, 804, 808
—, — chlorobenzene, 786, 787
—, — *m*-cresol, 788
—, — dichloroethane, 808, 809
—, — β,β′-dihalogenodiethyl ethers, 583
—, — di-iodofluoromethane, 737
—, — ethylene dichloride, 497
—, — methane, 280, 281
—, — olefins, 281, 614, 615
—, — olefin oxides, 567, 585, 587
—, — pentanes, 810
—, — trichloroacetyl glycol, 541
—, — wax acids, 979
—, use in aquolysis, 132
—, — cracking, 614
—, — estimation of sulphur, 1162
Ammoniacal silver, reaction with aldehydes, 885
—, silver from, 885
Ammonia-methane mixture, oxidation of, 871
Ammonium chloride, catalyst, hydration of ethylene, 288
—, —, olefin-carbon monoxide reaction, 446
—, —, reaction of monovinylacetylene and hydrochloric acid, 680
—, desulphurizing agent, 490
—, use in estimation of sulphur, 1162
—, — fermentation of sucrose, 547
Ammonium cyanide, nitriles from, 886
—, reaction with aldehydes, 886
Ammonium halides, catalysts, reaction of carbon monoxide and olefins, 626
Ammonium hydroxide, dechlorinating agent, 805
—, reaction with *o*-dichlorobenzene, 787
—, — nitromethane, 1096
Ammonium naphthenate, as coagulating agent, 1116
—, as demulsifying agent, 1116
Ammonium nitrate, catalyst, ammonia-chlorobenzene reaction, 787
—, for estimation of sulphur, 1161
Ammonium phosphotungstate, catalyst, hydration of ethylene, 288
Ammonium phthalate, phthalimide from, 958
Ammonium salts, emulsifying agents for asphalts, 1218
Ammonium sulphate, from sulphuric acid, 320
—, in cleaning agents, 1112
—, in tanning agents, 1078
Ammonium sulphide, as reducing agent, 1094
—, sulphur extraction with, 461
Ammonium sulphite, reaction with ethyl iodide, 819
—, removal of hydrogen sulphide by, 459
Ammonium sulphonate, as soap, 1069
Ammonium thiocyanate, in synthetic resins, 890
Ammonium thiosulphate, reaction with *n*-dodecyl iodide, 829
Ammonium tungstate, catalyst, hydration of acetylene, 712
Ammonolysis, of ethyl chloride, 808
Amyl acetate, in motor fuels, 1039
—, in rubber cement, 374
sec-Amyl acetate, ketene from, 437
ter-Amyl acetate, from isoamylene, 312
Amylacetylene, formation of, 722
ter-Amyl acid sulphate, hydrolysis of, 394
Amyl alcohol, as extraction agent, 1108, 1188, 1200
—, for absorption of olefins, 163
—, from amyl chloride, 755, 801-803
—, from petroleum ether, 853
—, in motor fuel, 1039
—, precipitation of resins with, 1188
—, reaction with benzene, 411
—, *see also* Pentanol
—, test for, 371
sec-Amyl alcohol, esterification of, 1081
—, from cracked gasoline, 388
—, from pentane, 859
—, reaction with naphthalene, 409
—, — naphthalene sulphonic acid, 409
—, refining ozocerite with, 409
ter-Amyl alcohol, action of sulphuric acid on, 417
—, from pentane, 859
—, from trimethylethylene, 387, 391
—, in refining crude oil, 415
—, pyrolysis of, 410
Amylamine, color stabilizer, 926
—, desulphurizing agent, 488
—, inhibitor of gum formation, 915
Amylbenzene, from phenylcyclopentane, 92
n-Amylbenzene, in gasoline, 144
ter-Amylbenzene, formation of, 411
Amyl bromide, reaction with calcium acetylide, 722
ter-Amyl bromide, hydrolysis of, 803
Amyl chloride, amyl alcohol from, 755
—, amylphenyl methyl ketone from, 448
—, from amylene, 511
—, from cracking gas, 302
—, hydrolysis of, 801-803
—, reaction with amyl oleate, 755
—, — calcium acetylide, 722
—, — oil, 812
—, — sodium cyanide, 822
ter-Amyl chloride, formation of, 310
—, pyrolysis of, 807
—, reaction with methyl pyromucate, 818
ter-Amyl chloroacetates, formation of, 313
ter-Amyl nitrate, from trimethylethylene, 623
—, saponification of, 623
Amylcyclohexane, cracking of, 137
Amylene, absorption in sulphuric acid, 310
—, amylene chlorohydrin from, 626
—, amyl ether from, 630
—, as anesthetic, 1263
—, benzoates from, 630
—, combustion of, 1004, 1005
—, from alcohols, 173
—, isopropyl ethylene glycol from, 548
—, pentane from, 630
—, reaction with benzoyl peroxide, 630
Amylene-1, reaction with chlorine, 511
—, — phosphorus pentachloride, 511
Amylene-2, reaction with chlorine, 512
Amylene chlorohydrin, from amylene, 626
Amylene dibromide, bromination of, 513
Amylene dibromide, preparation of, 513
1-Amylene dichloride, in synthesis of oils, 513
—, in dewaxing lubricants, 513
—, in insecticides, 513
—, preparation of, 511
—, *see also* Dichloropentane

ter-Amylenes, *ter*-amyl chloride from, 310
Amyl ether, from amylene, 630
ter-Amyl ethyl sulphide, preparation of, 472
Amyl formate, formation of, 312
Amyl mercaptan, in petroleum, 454
n-Amyl mercaptan, effect on color stability, 454
ter-Amyl nitrate, from trimethylethylene, 623
Amyl nitrite, action on methyl ethyl ketone, 452
—, reaction with trimethylethylene and nitric acid, 621
Amyl oleate, reaction with pentyl chloride, 755
ter-Amylphenol, as plasticizer, 604
—, preparation of, 412, 604
Amylphenyl methyl ketone, preparation of, 448
—, in paint removers, 448
sec-Amyl sulphate, hydrolysis of, 395
n-Amylsulphonic acid, valeric acid from, 1067
ter-Amyltoluene, formation of, 411
Anaerobic bacteria, action on fatty oils, 19
—, — proteins, 19
—, — waxes, 19
Anaerobic fermentation, in petroleum formation, 19, 20
Anesthetic, acetylene as, 1264
—, alkanes as, 1256
—, amylene as, 1263
—, chloroform as, 728
—, cyclohexane as, 1266, 1267
—, cyclopropane as, 1265, 1266, 1267, 1268
—, ethylene as, 1256-1261
—, propene as, 1263
Anethole, methylene ether from, 625
—, reaction with methyl hypobromite, 531
Aniline, as antioxidant, 917
—, as extraction agent, 30, 1205
—, as heat-transfer medium, 194
—, catalyst, co-polymerization of chloroprene, 681, 682
—, —, vinylacetylene-hydrogen sulphide reaction, 709
—, critical solution temperatures with, 1179
—, effect on octane number, 1032, 1033
—, from benzene, 260
—, from phenyl halides, 787, 810
—, in dewaxing oils, 379, 380
—, in motor fuels, 1039
—, in purification of alcohols, 408
—, inhibitor, paraffin oil oxidation, 907
—, reaction with acetylene, 719
—, — N-aminodiethylethanol, 569
—, — *β,β'*-dibromodiethyl ether, 583
—, — *β,β'*-dichloroethyl ether, 528, 583
—, — diketene, 442
—, — ethyl alcohol, 346
—, — ethyl chloride, 808
—, — 3-ethylpentene-2, 615
—, — fluorochloromethanes, 737
—, — 2-methylbutene-2, 615
—, — 3-methylpentene-2, 615
—, — monobromocyclohexane, 772
—, — monochlorocyclohexane, 768
—, — naphthenic acids, 1109
—, — nitrolic acids, 1094
—, — octene, 615
—, — pseudonitroles, 1094
—, — sulphonic acids, 1068
—, separation of sulphonates, 1072
—, stabilizing carbon tetrachloride, 733
Aniline black printing, use of triethanolamine in, 577
Aniline equivalent, definition of, 1024
—, knock rating by, 1024, 1025
Aniline hydrochloride, reaction with styrene, 614
Aniline point, characterization factor from, 1309
—, determination of, 30, 1150
Anisole, extraction of alcohols with, 360
—, reaction with isopropyl alcohol, 403
Anisotropic substance, definition of, 755
Anisyl alcohol, preparation of, 958
Anthracene, alkylated, from tars, 40
—, alkylation of, 595, 596
—, anthraquinone from, 952-954
—, antioxidant for gasoline, 916, 918, 927
—, by polymerization of cracking gas, 646
—, by pyrolysis of natural gas, 183
Anthracene, from benzene, 957
—, from 2,6-dimethylanthracene, 96
—, from ethylene, 77, 186
—, from isobutene, 85
—, from methane, 179, 180
—, from propane, 61
—, from sulphur-acetylene reaction, 720
—, from tars, 40
—, in acetylene black, 244
—, in petroleum coke, 145
—, oxidation of, 952-954
—, reaction with isoamyl chloride, 827
—, synthesis of coloring matter from, 215
—, synthetic oils from, 212
Anthracite, hydrogen from, 223
Anthranilic acid, color stabilizer, 926
Anthraquinone, cataylst, oxidation of toluene, 949
—, —, chlorination of benzene, 778
—, from anthracene, 952-954
—, reduction to anthranol, 570
Antiknock compounds, effect on ignition temperatures, 996
—, for gasoline, 1013, 1016-1022
Antiknock rating, relationship to structure of hydrocarbon, 141
Antiknock value, effect of peroxides, 924
Antimony, alloys of, in cracking, 112
—, catalyst, bromination of benzene, 790, 791
—, —, chlorination of acetylene, 743
—, —, dehydrogenation of paraffins, 158
—, —, oxidation of ethylene, 552
—, inhibitor, ethylene from methane, 54
—, —, formation of carbon, 191
Antimony chloride, catalyst, alkylation of phenols, 605
—, —, chlorination of ethylene, 495
—, —, — propene, 506
—, —, in cracking, 112
—, reaction with paraffins, 1102
Antimony chlorides, catalysts, bromination of toluene, 795
Antimony dichlorotrifluoride, catalyst, fluorination of carbon tetrachloride, 733, 734
Antimony fluorochlorides, catalysts, in fluorination, 735, 736
Antimonyl tartrate, corrosion inhibitor, 375
Antimony oxide, catalyst, oxidation of aromatics, 942
—, —, — olefins, 553
—, for hydrogen sulphide removal, 458
Antimony pentachloride, catalyst, chlorination of hexane, 757
—, —, — methane, 726
—, —, fluorination of benzene, 792
—, —, — carbon disulphide, 737
—, —, — carbon tetrachloride, 733-736
—, —, — paraffin wax, 759
—, —, — trichloroethane, 747
—, —, polymerization of isobutene, 204
—, —, — styrene, 647
—, for identification of paraffins, 31, 32
—, reaction with gasoline, 32, 1243
Antimony salts, catalyst, fluorination of carbon tetrachloride, 736, 737
Antimony trichloride, catalyst, chlorination of benzene, 778
—, —, condensation of cyclohexane, 205
—, —, esterification of olefins, 302
—, —, in fluorination, 735
—, reaction with hexachloroethane, 748
Antimony trifluoride, catalyst, fluorination of paraffin wax, 759
—, reaction with carbon tetrachloride, 733, 734, 736
—, — methylene chloride, 734
—, trichlorofluoromethane from, 734
Antioxidants, effect on allyl bromide-hydrogen bromide reaction, 315
—, evaluation of, 919, 920
—, for cyclohexene, 907
—, for fats, 914
—, for gasoline, 912, 914-919, 927
—, for hydrogenated oils, 914
—, for paraffin oils, 907
—, for rubber, 855

Antioxidants, for transformer oil, 941
—, for white oils, 937, 940
—, from alkylated phenols, 604
—, natural, in gasoline, 927
—, preparation from lead tetra-alkyls, 823
—, — sulphur, 486
—, reactions with sulphuric acid, 919
—, solvents for, 919
Aqueous content, of crude oil, 10
Aquolization, process of, 131
—, use of ammonia in, 132
—, — magnesium chloride in, 133
—, of emulsions, 133
Aralkyl halides, fluorides from, 735
—, reaction with alcoholates, 825
Aralkyl thiocarbonates, preparation of, 487
Argon, depressant, decomposition of ethylene oxide, 554
—, effect on acetylene polymerization, 267
—, — ignition temperature, 997, 998
—, — inflammability limits, 984, 985
—, — knocking, 1011, 1012
—, — polymerization of butadiene, 650
—, estimation of, 1147, 1148
Argon-nitrogen ratio, in natural gas, 22
Aromatic acids, hydroxy, reaction with olefins, 607
Aromatic alcohols, stabilized by triethanolamine, 577
Aromatic aldehydes, reaction with ketene, 438
Aromatic amines, from chlorobenzenes, 782
Aromatic compounds, extraction of, 30
—, in kerosene, 36
Aromatic hydrocarbons, bromination of, 31
—, separation from gasolines, 30
—, separation from naphthenes, 31
—, separation from paraffins, 31
—, solvents for, 30
Aromaticity, of lubricating oils, 44
Aromatics, action of corona discharge on, 260
—, — silent discharge on, 210, 259, 260
—, aniline equivalents of, 1024
—, antiknock qualities of, 141, 1016
—, by hydrogenation of paraffin wax, 179-181
—, by pyrolysis of gas oil, 178
—, — natural gas, 182, 183
—, — petroleum distillates, 177, 178
—, characterization factor of, 1307
—, combustion of, 999
—, dealkylation of, 208
—, effect of lead tetraethyl on, 1019
—, effect on knock rating, 1024, 1025
—, entropy of formation, 1284-1286
—, estimation, by nitration, 1154
—, —, by oxidation, 1155
—, —, by sulphonation, 1154
—, —, with trinitrophenol, 1154, 1155
—, factors influencing yield of, 188
—, formation of coke from, 109
—, free energy of formation, 1284-1286
—, from acetylene, 89
—, from aliphatic hydrocarbons, 73, 188, 189
—, from asphalt-base spindle oil, 36
—, from butane, 181, 190
—, from carbon monoxide and hydrogen, 1243
—, from cyclohexane hydrocarbons, 178
—, from cycloparaffins, 185, 186, 196
—, from ethyl alcohol, 342
—, from ethylene, 77, 185, 636-639
—, from Gasol, 1255
—, from hydroaromatics, 33
—, from Kogasin, 1252
—, from methane, 179, 180, 181
—, from naphtha oxidation, 876
—, from naphthalene, 36
—, from naphthenes, 843
—, from olefins, 184, 185, 190, 646
—, from paraffins, 141, 186, 187
—, from phenanthrene, 37
—, from pinene, 88
—, from propane, 60, 181, 182
—, from propene, 639
—, heat of formation, 1284-1286
—, improvement of gasolines by, 135
Aromatics, in gasoline, 28, 32, 143
—, —, estimation of, 1149, 1150
—, in petroleum, 13, 17, 31, 32, 1149
—, molal entropy of, 1284-1286
—, —, effect of structure on, 1289, 1290
—, nitration of, 1096, 1154
—, octane numbers of, 1028
—, olefins from, 148
—, oxidation of, 942-961, 1155
—, peroxides from, 922
—, pyrolysis of, 95, 96, 148
—, reaction with carbon monoxide, 1099
—, — chlorinated Kogasin, 1253, 1254
—, — chlorosulphonic acid and naphthenic acids, 1118
—, — ethylene oxide, 563
—, — halogenated olefins, 592, 593
—, — Kattwinkel's reagent, 1150
—, — olefins, 591-598
—, separation, by sulphuric acid, 1081
—, —, with silica gel, 1155
—, stability, effect of structure on, 1285
—, sulphonation of, 1154
—, γ-sulphonic acids from, 1065
—, thermal stability of, 95, 101, 108
—, voltolization of, 261
Arsenic, acid salts, catalysts, reaction of olefins and carbon monoxide, 626
—, catalyst, dehydrogenation of hydrocarbons, 158
—, —, preparation of ethylene oxide, 552
Arsenic acid, catalyst, oxidation of ethylene, 894
—, —, carbon monoxide-methyl alcohol reaction, 1050
Arsenic chloride, catalyst, polymerization of isobutene, 204
Arsenic oxide, catalyst, olefin oxidation, 553
—, for hydrogen sulphide removal, 458
Arsenic trichloride, catalyst, condensation of cyclohexane, 205
—, reaction with cyclohexane, 1102
—, — dioxane, 580
Arsenic trifluoride, catalyst, polymerization of isobutene, 642
Arsenic trioxide, antioxidant, cyclohexene, 907
Arsenious acid, in oxidation of paraffin wax, 973
—, reaction with ethylene dibromide, 505
—, — polyglycols, 545
Aryl amines, condensation with conjugated diolefins, 691
Aryl-amino-naphthalenes, as antioxidants, 918
Aryl arsine oxides, as antioxidants, 918
Aryl cyanamides, for stabilizing carbon tetrachloride, 730
β-Arylethyl alcohols, formation of, 563
Aryl halides, condensation with conjugated diolefins, 691, 693, 694
Aryl stibine oxides, as antioxidants, 918
Aryl sulphonic acids, for refining gasoline, 930
Asbestos, in production of carbon black, 240
Asbestos, platinized, dehydrogenation catalyst, 1150
Ascaridole, definition of, 316
—, effect on hydrogen bromide-isobutene reaction, 317
—, — pentene-2-hydrogen bromide reaction, 318
—, — propene-hydrogen bromide reaction, 316
Ascoloy, catalyst, pyrolysis of olefins, 76
Ash, from petroleum, 46
—, —, composition, 48
Aspergillus niger, action on glycols, 549
Asphalt, acetone solvent for, 434
—, adhesion energy of, 1213
—, adsorption by bleaching earths, 1155
—, as colloidal system, 1195, 1196, 1197, 1198
—, asphaltogenic acids from, 1194
—, benzine precipitant for, 1196
—, by cracking oils, 1139
—, by oxidation of oils, 1043
—, classification of, 1210
—, components of, 1186, 1192-1194
—, decolorizing agents for, 1192
—, ductility determination of, 1207, 1208
—, emulsifying agents for, 1216, 1217, 1218
—, estimation of, 1155, 1156, 1191

Asphalt, estimation of paraffin in, 1199
—, extractants for, 1202
—, extraction of oils from, 1200
—, extraction with acetone, 1193
—, flocculating agents for, 1196
—, fluidity index of, 1210
—, formation of, 21
—, from cracked distillates, 675
—, from crude oils, 1202
—, from petroleum, 1205
—, from petroleum acids, 1112
—, from pyroschists, 145
—, hard, from oils, 1188
—, —, precipitation with benzine, 1188
—, in petroleum, 13, 1186
—, in road construction, 1211
—, isolation of oily portion from, 1187
—, methods of applying coatings of, 1214
—, oxidation of, 1202-1205
—, oxidized, olefin content of, 1206
—, —, treatment with benzine, 1205
—, —, — propane, 1205
—, oxygen absorption rate of, 1203
—, penetration, determination of, 1208
—, penetration-temperature relation of, 1211
—, physical properties of, 1206
—, precipitation from oils, 935, 1201
—, precipitation of carbenes from, 1193
—, precipitation with ethane, 1201
—, — propane, 1200, 1201
—, refining of, 1192
—, softening point-penetration index of, 1208, 1209
—, solubility in carbon disulphide, 1200
—, spreading coefficient of, 1213
—, susceptibility factor of, 1210
—, uses for, 1192, 1213, 1214
—, viscosity determination of, 1206, 1207
—, viscosity reduction by phenols, 1218
Asphalt compositions, altering flowing qualities of, 1213, 1214
—, — hardness of, 1213, 1214
Asphalt emulsions, breaking tests for, 1220, 1221
—, classification of, 1219, 1220
—, effect of alkali on, 1215
—, — calcium chloride on, 1215
—, — sodium chloride on, 1216
—, — trisodium phosphate on, 1219
—, estimation of water in, 1221
—, measuring particle size of, 1221
—, preparation of, 1216, 1217
—, stability of, 1215
—, stabilization of, 1218
—, test for demulsibility of, 1220, 1221
—, use of clay in, 1219
—, uses for, 1220
—, viscosity of, 1216
Asphaltenes, asphaltogenic acids in, 1186
—, by oxidation of resins, 1189
—, composition of, 1190
—, effect of heat on, 1202
—, — sulphur compounds on formation, 1190
—, — water vapor on formation, 935
—, estimation of, 1192, 1193
—, formation in lubricants, 930, 932
—, from lubricating oil, 855
—, from naphthenes, 195
—, hydrogenation of, 1192
—, in alkali sludge, 1105
—, in asphalt colloidal systems, 1197, 1198
—, in petroleum, 1189, 1190
—, lyophilic properties of, 1190
—, lyophobic properties of, 1190
—, oxidation of, 1191, 1203
—, precipitation of, 1191, 1192
—, reaction with chlorosulphonic acid, 1191
—, — halogens, 1191
—, — nitric acid, 1191
—, — perbenzoic acid, 1191
—, — sulphuric acid, 1191
—, solvents for, 1190
Asphalt formation, in paraffin-base oils, 1199
Asphaltic hydrocarbons, from paraffin hydrocarbons, 18
Asphaltic oils, estimation, by ultraviolent light, 1150
—, treatment with propane, 1200, 1201
Asphaltic resins, from petrolenes, 1202
Asphaltic substances, precipitated by propane, 46
Asphaltite, vanadium in, 46
Asphaltogenic acids, formation in petroleum, 1194, 1195
—, from mineral oils, 1195
—, from transformer oils, 1195
—, in asphalts, 1186, 1194
—, properties of, 1195
—, separation from asphalts, 1194
—, toxic effect on plants, 1195
Asphalt oil, reaction with sulphur, 467
Asphalt paper, use of asphalts in, 1192
meso-Atioporphyrin, in oil shale, 20
Atomic hydrogen, action on metallic mirrors, 51
—, formation during pyrolysis, 51, 53
Atropic acid, *see* α-Phenylacrylic acid
Auto-destructive alkylation reaction, 200
Auto-ignition, of cyclohexadiene, 1017
—, of cyclohexene, 1017
—, of hexane, 1017
Autopolymerization, of butadiene, 692
Autoxidation, definition of, 905
—, effect on gum deposition, 855
—, — storage of gasoline, 855
—, mechanism of, 856
—, of cyclohexene, 907
—, of decalin, 907
—, of 1,4-dimethylcyclohexane, 907
—, of gasoline, 907
—, of lubricating oil, 855, 930
—, of naphthenic alcohols, 1118
—, of oxygen-containing compounds, 922
—, of phenylcyclopentane, 907
—, of tetralin, 905
Aviation lubricants, from kerosene distillates, 211
Aviation fuel, knock rating of, 1027
Azeotropes, associated with aromatics, 30
—, in gasoline, 30
Azeotropic distillation, of ethyl alcohol, 328, 329
Azeotropic mixture, of acetylene and ethane, 30
—, resolution of, 30
—, use in fractionation, 1140, 1141
Azobenzene, reduction to aniline, 570
Azomethane, decomposition of, 51
—, effect on ethylene polymerization, 636
Azoxybenzene, as antioxidant, 917

B

Bacteria, effect on petroleum origin, 19
Bactericides, from ethylene glycol esters, 540
Bacteriostatic agents, from ethylene glycol esters, 540
Baffles, use in pyrolysis, 150, 151
Barium boro-phosphate, catalyst, hydration of ethylene, 285
—, —, hydration of propene, 292
Barium carbonate, catalyst, hydrolysis of acetaldehyde, 422
—, —, — ethylene dichloride, 533
—, —, pyrolysis of ethyl acetate, 423
—, —, — ethyl alcohol, 422
Barium chloride, catalyst, chlorination of propene dichloride, 507
—, —, dechlorination of propyl chloride, 806
—, —, esterification of ethylene, 302
—, —, ethylene oxidation, 894
—, —, pyrolysis of butene dichloride 510
—, inhibitor, dechlorination, 805
—, removal of gum-forming compounds with, 216
Barium compounds, catalysts, hydration of acetylene, 714
Barium hydroxide, catalyst, condensation of acetone, 427
—, —, hydrolysis of tertiary bromides, 413
—, reaction with isopropyl hydroperoxide, 382
—, — polyethylene sulphone, 617
—, — propene sulphone, 617

Barium naphthenate, catalyst, oxidation of paraffin wax, 971
—, in inks, 1117
Barium nitrate, extraction with isopropyl alcohol, 375
Barium oxide, catalyst, hydration of acetylene, 714
—, —, pyrolysis of alcohols, 340
—, —, reduction of carbon monoxide, 1228, 1240
Barium peroxide, catalyst, oxidation of crude oil, 1047
Barium phosphate, catalyst, hydration of propene, 292
Barium sulphinates, from polyethylene sulphone, 617
Barium sulphocyanide, catalyst, reaction of cellulose and alkene oxides, 588
Bauxite, catalyst, decomposition of ether, 334, 335
—, —, pyrolysis of still gas, 223
—, desulphurizing agent, 398, 478, 488
—, in cracking of oils, 112
—, in hydrolysis of acid liquors, 327, 364
—, in refining kerosene, 925
—, in reforming gasoline, 189
Beeswax, in candle wax, 543
Beeswax substitutes, from wax acids, 970
Beet pulp, in cracking, 111
Bentonite, catalyst, hydrolysis of chlorobenzene, 782
—, catalyst, polymerization of olefins, 666
—, in asphalt emulsions, 1219, 1220
Benzal chloride, benzaldehyde from, 794
—, benzene from, 794
—, from toluene, 794
—, reaction with dimethyl ether, 794
—, — sodium sulphite, 794
Benzaldehyde, as antiknock, 1017
—, autoxidation of, 905
—, benzyl alcohol from, 958
—, by oxidation of benzyl-2-chlorophenyl ketone, 452
—, extraction agent, 44
—, —, stilbene, 895
—, — toluene, 947, 948, 954
—, from benzene, 949, 957
—, from benzal chloride, 794
—, from benzyl chloride, 957
—, from diethyl phthalate, 952
—, from dimethyl phthalate, 952
—, from nickel phthalate, 952
—, from phthalic anhydride, 950
—, from zinc phthalate, 952
—, oxidation of, 899, 957
Benzamide, acetylation of, 438
Benzanthrone-2-aldehyde, from 2-methylbenzanthrone, 957
Benzene, acetylation of, 439
—, acetylene from, 95, 259
—, action of aluminum chloride on, 207
—, — brush discharge on, 260
—, — silent discharge on, 259, 260
—, — Telsa discharge on, 260
—, and sulphur dioxide, extraction agent, 41
—, aniline from, 260
—, anthracene from, 957
—, as antiknock, 1016, 1017
—, as blending agent, 1035
—, as dehydrating agent for alcohols, 327, 328, 364, 408
—, as extraction agent for acetone peroxide, 432
—, — carbon black, 251
—, — lecithin and fat, 728
—, — mazout, 1188
—, — naphthenic acids, 1108
—, — resins, 216
—, as solvent, 372, 435, 446, 447, 742, 919, 1060
—, azeotropic mixture with isopropyl alcohol, 369
—, benzaldehyde from, 949, 957
—, benzene hexachloride from, 781
—, benzoic acid from, 957
—, benzoquinone from, 944, 953
—, biphenyl from, 206, 207, 259, 260
—, bromination of, 790, 791
—, bromobenzene from, 791
Benzene, by cracking of cylinder oil, 137
—, — gasoline, 136
—, — kerosene, 137, 144
—, — paraffin wax, 138
—, — *n*-tetradecane, 1297
—, by oxidation of acenaphthalene, 946
—, — cyclohexane, 1041
—, — naphthalene, 946
—, by polymerization of acetylene, 266, 703
—, — cracking gas, 646
—, by pyrolysis of alcohol, 177
—, — 2,6-dimethylanthracene, 96
—, — ethylbenzene, 96
—, — ethylcyclohexane, 93
—, — ethylene, 77, 186
—, — gas oil, 178
—, — *n*-hexane, 71, 73
—, — isobutene, 85
—, — methane, 179
—, — 2-pentene, 87
—, — propane, 60, 182
—, — *p*-xylene, 96
—, catalyst, cracking processes, 214
—, —, esterification of propene, 306
—, chlorination of, 777-781
—, chlorobenzene from, 778, 780, 950
—, combustion of, 1003-1005
—, —, effect of temperature on, 1005
—, cyclohexane from, 1298
—, decomposition of, 191, 192, 199
—, —, photochemical, 207
—, detection in alcohol, 354
—, deuterium in, 206
—, dibromobenzene from, 791
—, *p*-dichlorobenzene from, 781
—, dihydrobiphenyl from, 259
—, diphenylamine from, 260
—, diphenylcyclohexane from, 207
—, effect of tetraethyl lead on, 1021, 1022
—, effect on decomposition of acetone, 450
—, enthalpy-pressure-temperature relations, 1333
—, estimation by colorimetry, 1148
—, — in blended fuels, 1185
—, — of wax in asphalt, 1155
—, ethylbenzene from, 206, 207
—, explosive characteristics of, 1011
—, fluorination of, 791, 792
—, free energy of formation, 1225, 1226
—, —, effect of temperature on, 1295
—, from carbon monoxide and hydrogen, 1243
—, from benzal chloride, 794
—, from *n*-butylbenzene, 208
—, from cyclohexane, 92
—, from ethylbenzene, 208
—, from isopropylbenzene, 208
—, from toluene, 208
—, from xylene, 208
—, hexabromobenzene from, 790, 791
—, hydrogen from, 259
—, hydrogenation of, destructive, 207
—, —, free energy change, 1298
—, —, —, effect of temperature on, 1298, 1299
—, hydroquinone from, 942
—, ignition temperature of, 987, 988, 1000
—, in acetylene black, 244
—, in crude oil, 31
—, in gasoline, 34, 144, 196
—, in insecticides, 733
—, in lubricating oil, 215
—, in motor fuels, 1039
—, in paint remover, 790
—, in wet gas, 22
—, inflammability limits of, 980-982, 985
—, maleic acid from, 944
—, maleic anhydride from, 944, 945
—, 1-methyl-3-phenylcyclopentane from, 207
—, molal entropy of, 1289, 1290
—, nitration of, 1091
—, oxidation of, 850, 855, 931, 942, 944, 945, 953
—, pentabromobenzene from, 790, 791
—, phenol from, 260, 942
—, phenylcyclohexane from, 207
—, pyrolysis of, 95

Benzene, reaction with acetylene, 718
—, — amyl alcohols, 411
—, — amyl chloride and acetyl chloride, 448
—, — benzoyl chloride, 815, 816
—, — butene-1, 591
—, — *sec*-butyl alcohol, 402
—, — *ter*-butyl alcohols, 411
—, — carbon dioxide, 260
—, — carbon monoxide, 949, 957
—, — chlorinated decane, 758
—, — chlorinated Kogasin, 1253, 1254
—, — chlorinated paraffin wax, 758
—, — chlorine monoxide, 781
—, — cracking gas, 593, 594
—, — cyclohexene, 592, 595
—, — cyclopropane, 596
—, — deuterium oxide, 260, 273
—, — dichloropentamethylenetetramine, 779
—, — diisobutylene, 592
—, — diisopropyl sulphate, 597, 598
—, — dodecene, 591
—, — ethylene, 594, 595, 597
—, — ethylene dichloride, 815
—, — ethylene oxide, 563
—, — *n*-hexane, 602, 603
—, — hexene, 591, 598
—, — hydrogen chloride, 950
—, — isobutene, 591, 594, 596
—, — isopropyl alcohol, 382, 383, 401, 402
—, — methyl hypobromite, 531
—, — nonene, 591
—, — octene, 591
—, — oleic acid, 815
—, — pentene, 591
—, — propene, 591-593, 595-597
—, — propyl chloride, kinetics of, 815
—, — steam, 273
—, — stilbene, 207
—, — sulphur, 468
—, — trichlorobenzyl chloride, 816
—, — *n*-tridecane, 1254
—, — tri-isobutylene, 592
—, — 2,2,4-trimenthylpentane, 602, 603
—, separation from coke-oven gas, 165
—, separation of acids with, 967, 968
—, sulphonation of, 669
—, tetrabromobenzene from, 790, 791
—, toluene from, 206
—, tribromobenzene from, 791
—, use in dehydrogenation of borneol, 444
—, — dehydrogenation of isopropyl alcohol, 420
Benzene-gasoline blends, octane number of, 1251
—, stabilization of, 915
Benzene hexachloride, from benzene, 781
—, from petroleum-coal distillate, 781
Benzene homologues, as antiknocks, 1018
—, viscosity of, 38
Benzenlsulphonic acid, as dehydrating agent, 406
—, as wetting agent, 1076
—, catalyst, isomerization of 1-butene, 82
—, —, esterification of propene, 308
—, —, polymerization of formaldehyde, 579
—, reaction with olefins, 314
Benzidine, as antioxidant, 917
Benzine, action of silent discharge on, 263
—, dehydration agent for ethyl alcohol, 329
—, — isopropyl alcohol, 364
—, extraction agent for oils, 1200
—, — oxidized asphalt, 1205
—, — oxidized wax, 975
—, — polymerized hydrocarbons, 397
—, flash point of, 988
—, flocculating agent for asphalt, 1196
—, from hydrogen and carbon monoxide, 155
—, precipitant for asphalt, 935
—, — for asphaltenes, 1191, 1192
—, — in asphalt analysis, 1196
—, pyrolysis of, 155
—, reaction with acetyl chloride, 445, 1099
—, refining with aluminum chloride, 263
—, — ferric chloride, 263, 929
—, — sulphuric acid, 263
—, separation of acids with, 967, 968
Benzine solvent for methane, 234
—, synthesis of, 168
Benzoates, from amylene, 630
Benzoic acid, adsorption by carbon black, 252
—, by oxidation of acetophenone, 450
—, — benzene, 957
—, — benzyl alcohol, 851
—, — benzyl chloride, 957
—, — naphthalene, 950-952
—, — nickel phthalate, 952
—, — phenylacetylene, 904
—, — phthalic anhydride, 950-952
—, — toluene, 948-950
—, — zinc phthalate, 952
—, effect on hydrogenation of olefins, 900
—, from benzoyl peroxide, 630
—, hydroxy, reaction with propane, 609
—, reaction with α-chloroethylbenzene, 805
—, — isopropyl alcohol, 376
—, — naphthalene, 448
—, — propene, 308
—, solubility of, 959
Benzoic peroxide, catalyst, reaction of propene and sulphur dioxide, 617
Benzoin, oxidation of, 953
Benzol-alcohol-gasoline blends, as motor fuels, 1038
Benzol, as blending agent, 1035
—, as dewaxing agent, 433
—, by pyrolysis of methane, 180
—, — natural gas, 171, 183
—, peptizing agent for asphalts, 1196
—, reaction with maleic anhydride, 690
—, refining with sulphuric acid, 184
—, separation of conjugated diolefins from, 679
—, — with carbon, 182
Benzol-gasoline blends, as motor fuels, 1038
Benzonitrile, from ketene-benzamide reaction, 438
Benzophenone, by oxidation of diphenylmethane, 943, 957
—, — triphenylmethane, 943
—, reaction with sulphur, 468
Benzophenone, use in polyprene, 681
Benzoquinone, by oxidation of benzene, 944, 953
—, — naphthalene, 951
—, hydroquinone from, 953
—, reaction with butadiene, 699
—, — diolefins, 175
—, reduction of, 953
Benzotrichloride, from toluene, 794
—, reaction with phthalic anhydride, 794
—, — sulphonic acids, 794
Benzotrifluoride, from benzotrichloride, 735
Benzoylation, of hexamethylenetetramine, 888
Benzoylbenzoic acid, alkoxyalkyl ester, as plasticizing agent, 544
Benzoyl chloride, from phthalic anhydride, 952
—, reaction with benzene, 815, 816
Benzoyl peroxide, benzoic acid from, 630
—, catalyst, oxidation of naphtha, 876
—, —, polymerization of styrene, 647
—, effect on hydrogenation of olefins, 900
—, — propene-hydrogen bromide reaction, 316
—, — propene-hydrogen chloride reaction, 306
—, — styrene-hydrogen bromide reaction, 318
—, reaction with amylene, 630
Benzoyl persulphide, preparation of, 480
Benzyl acetate, from benzyl chloride, 794
Benzylacetylene, from phenylallene, 807
Benzyl alcohol, as antiknock, 1017
—, benzoic acid from, 851
—, from benzaldehyde, 958
—, oxidation of, 851
—, solvent properties of, 1179
5-Benzylamino-2-cresol, antioxidant for gasoline, 916
Benzylaminophenol, as antioxidant, 913, 916
Benzyl bromide, from toluene, 795
Benzyl chloride, benzaldehyde from, 957
—, benzoic acid from, 957
—, benzyl acetate from, 794
—, corrosion inhibitor, 794
—, from toluene, 793, 794
—, oxidation of, 957

Benzyl chloride, reaction with acetic anhydride, 794
—, — ethylene glycol, 543
—, — sodium acetate, 794
Benzyl-2-chlorophenyl ketone, benzaldehyde from, 452
Benzyl disulphide, antioxidant for transformer oil, 941
Benzylidene-amino-phenol, antioxidant for gasoline, 916
Benzyl mercaptan, reaction with carbon disulphide, 487
Benzylmethylaminophenol, antioxidant for gasoline, 916
Benzylpyridinium chloride, catalyst, preparation of cellulose derivatives, 588
Benzyl sulphide, corrosion inhibitor, 486
Beryllium bromide, catalyst, bromination of benzene, 791
Beryllium chloride, catalyst, alkylation of aromatics, 596
—, —, polymerization of isobutene, 204, 642
Beryllium compounds, catalysts, oxidation of alcohols, 1051
Beryllium oxide, catalyst, decarboxylation of phthalic anhydride, 950
—, —, methane-steam reaction, 279
—, —, oxidation of aromatics, 942
—, —, reduction of carbon monoxide, 1228
Beryllium phosphate, catalyst, hydration of ethylene, 287
—, —, hydration of propene, 293
Beryllium sulphate, promoter, hydration of ethylene, 283
Biacetyl, flavoring agent, 708
—, from 2,3-butene glycol, 548
—, from methyl ethyl ketone, 452
—, from vinylacetylene, 708
Bibenzyl, from benzene and acetylene, 718
—, from benzene and ethylene oxide, 563
—, from stilbene, 207
—, molal entropy, 1289
Bichloride of mercury, *see* Mercuric chloride
Bicyclic naphthene hydrocarbons, derivatives of, 10
Bicyclohexyl, cracking of, 137
—, preparation of, 205, 767
Biphenyl, as heat-transfer medium, 28, 191, 193, 194, 420
—, from benzene, 95, 191, 206, 207, 259, 260
—, in lubricants, 194
—, in motor fuel, 1039
—, molal entropy, 1289
—, reaction with chlorinated paraffin wax, 817
Biphenyl homologues, viscosity of, 38
Biphenylene, from benzene, 259
Bis-(2-chloroethyl) ether, as dewaxing agent, 434
Bis-(β-methoxyethyl) methylene ether, preparation of, 582
Bismuth, catalyst, bromination of benzene, 790, 791
—, —, isopropyl alcohol from propene, 360
—, —, oxidation of ethylene, 552
Bismuth bromide, catalyst, esterification of alcohol, 345
—, —, — propene, 308
Bismuth chloride, catalyst, chlorination of ethylene, 495
—, —, — propene, 506
—, —, esterification of alcohol, 345
—, —, — olefins, 301, 302, 306, 311, 316
—, —, reaction of olefins and chloroethers, 613
—, —, — propene and iodine, 506
Bismuth halides, catalysts, dehydrogenation of hydrocarbons, 158
—, —, reaction of carbon monoxide and olefins, 625, 626
Bismuth ions, catalysts, nitration of toluene, 954
Bismuth oxide, catalyst, decarboxylation of phthalic anhydride, 951
—, —, oxidation of aromatics, 942, 950
—, —, reaction of benzyl chloride and acetic anhydride, 794
—, effect on ignition temperature, 1000
Bismuth phosphate, catalyst, isopropyl acetate from propene, 308
Bismuth salts, promoters, oxidation of toluene, 950
Bismuth sulphate, catalyst, isopropyl acetate from propene, 308
Bismuthyl chloride, catalyst, ethyl alcohol-hydrogen chloride reaction, 345
Bisnitrosates, from olefins, 620
Bisulphates, catalysts, dimerization of ethylene oxide, 579
Bituminous emulsions, coagulation of, 1116
Bivinyl, *see* Butadiene
Black kontakt, as demulsifying agent, 1075
—, definition of, 1075
Bleaching agents, sulphuric esters of ethanolamines as, 578
Bleaching clay, in decolorizing resins, 216
Bleaching earths, catalysts, polymerization of diolefins, 171
—, —, oxidation of methane, 882
—, in asphalt compositions, 1214
—, separation of asphalts in oil, 1155
Bleaching powder, use in purification of acetylene, 170
Blended motor fuels, 1034-1040
Blending agents, for gasoline-alcohol-benzol blends, 1038
—, for gasoline-alcohol blends, 1035
Blending octane number, definition of, 1025, 1029
—, comparison with octane numbers, 1026
—, knock rating by, 1025-1027
—, of 1-heptene, 1026, 1027
Blood, effect of ethylene on, 1260, 1261
Blood pressure, effect of cyclopropane on, 1265
—, effect of ethylene on, 1261
Blood sugar, effect of ethylene on, 1260, 1261
Blood urea, effect of ethylene on, 1261
Boiling point, critical pressure from, 1314, 1315, 1316
—, heat of vaporization from, 1325, 1327
—, molal average, characterization factor from, 1307, 1309, 1310
—, —, critical pressure from, 1318
—, —, critical temperature from, 1312, 1313
—, —, estimation of, 1308, 1309
—, —, molecular weight from, 1311
—, 50 per cent, critical temperature from, 1311, 1312
Bone charcoal, catalyst, cracking of petroleum, 111
Bone fat, in asphalt emulsions, 1216
Bone grease, reaction with ethylene glycol, 540
Boost pressure, definition of, 1027
Borax, extractant for butadiene, 174
Borates, estimation with isopropyl alcohol, 375
Borax, catalyst, cracking of petroleum, 111
Boric acid, catalyst, oxidation of ethylene, 894
—, —, — paraffin wax, 973
—, —, polymerization of olefins, 634
—, —, pyrolysis of methane, 227
—, corrosion inhibitor, 574
—, reaction with diethylene glycol monoethyl ether, 545
Boric acid salts, catalyst, hydration of ethylene, 288
—, —, reaction of olefins and carbon monoxide, 626
Borneol, as blending agent, 1035
—, dehydrogenation of, 444
Boron, catalyst, pyrolysis of gaseous hydrocarbons, 189
Boron carbide, catalyst, oxidation of toluene, 948
Boron fluoride, as decolorizing agent, 1192
—, as refining agent, 719
—, catalyst, esterification of acids, 314
—, —, — olefins, 308
—, —, — acetylene, 717
—, —, vinylacetylene-alcohol reaction, 706
—, —, vinylacetylene-carboxylic acid reaction, 706
—, —, voltolization, 262
—, *see also* Boron trifluoride
Boron oxide, catalyst, hydrogen-carbon monoxide reaction, 661
—, —, oxidation of aromatics, 942

Boron phosphate, as antiknock, 115
—, catalyst, carboxylic acids from olefins, 446
—, —, hydration of ethylene, 284, 287
—, —, — propene, 293
—, —, polymerization of olefins, 288
—, —, reaction of olefins and carbon monoxide, 626
—, preparation of, 115
Boron trifluoride, catalyst, alkylation of alcohols, 606
—, —, — aromatics, 596, 597, 598
—, —, — hydroxy aromatic acids, 607, 609
—, —, — paraffins, 598, 599, 1301
—, —, — phenols, 403, 605
—, —, condensation of dichlorobutenes, 685
—, —, — isopropyl cresyl ethers, 383
—, —, — isopropyl phenyl ether, 383
—, —, cracking processes, 112
—, —, esterification of isopropyl alcohol, 376
—, —, — propene, 376
—, —, polymerization of Kogasin, 1255
—, —, — olefins, 195, 204, 210, 635, 636, 642, 649
—, —, reaction of butylacetylene and mannitol, 724
—, —, — ethylene oxide and isopropyl alcohol, 557
—, —, — methyl alcohol and alkylacetylene, 722
—, —, — olefins and chloroesters, 614
—, —, — propene and salicylic acid, 308
—, in refrigerants, 738
—, *see also* Boron fluoride
Brake fluid mixtures, preparation of, 539, 540, 542, 546, 1114
Brass, catalyst, cracking of ethylene, 172
—, —, dehydrogenation of alcohols, 420
—, —, oxidation of kerosene, 965
—, for removal of sulphur compounds, 397
—, use in refining gasoline, 668
Brass spelter, catalyst, oxidation of 2-methyl-1-butene-3-ol, 444
Bromide-bromate method, for estimation of alkadienes, 1144, 1152
—, — cycloalkenes, 1152
—, — olefins, 1152
ter-Bromides, reaction with alkalies, 413
Bromination, estimation of alkadienes, 1152
—, — cycloalkenes, 1152
—, — olefins, 1142, 1143, 1150, 1152
—, of acetone, 430
—, of benzene, 790, 791
—, of butadiene, 683-685
—, of butadiene sulphones, 694
—, of chlorotoluenes, 795
—, of cyclohexane, 769, 770
—, of cyclohexanol, 770
—, of cyclohexene, 770
—, of cyclopentadiene, 684, 700
—, of cyclopentene, 764
—, of cyclopropane, 761
—, of cyclopropene, 761, 762
—, of dicyclopentadiene, 700
—, of dimethylcyclohexene, 775
—, of ethane, 747
—, of ethylene, 501-503
—, of hexene, 146
—, of liquid paraffins, 759
—, of menthane, 776
—, of methylcyclohexene, 775
—, of monofluorocyclohexane, 774
—, of pentene, 146
—, of polyethylene sulphone, 617
—, of toluene, 794, 795
Bromine, estimation of olefins, 1124, 1142-1144, 1152
—, — sulphur, 1161
—, from sea water, 504
—, inhibitor, polymerization of chloroprene, 681
—, separation of amylene with, 174
—, — piperylene with, 174
Bromine trifluoride, as fluorinating agent, 736
α-Bromo acids, from petroleum acids, 447
Bromoacetamide, reaction with cyclohexa-1,3-diene, 531
2-Bromoazobenzene, condensation with cyclopentadiene, 693
Bromobenzene, *p*-aminobiphenyl from, 787
—, aniline from, 787
—, diphenylamine from, 787
—, from benzene, 791
—, phenyl from, 827
—, reaction with potassium amide, 787
—, — sodium, 827
—, triphenylamine from, 787
1-Bromobutadiene, reaction with hydrogen bromide, 686
2-Bromobutadiene, preparation of, 680, 681
1-Bromobutane, from 1-butene, 317
2-Bromobutane, from 1-butene, 317
—, hydrolysis of, 799, 800
Bromobutanes, olefins from, 806
1-Bromo-2-butene, from butadiene, 686
2-Bromo-2-butene, from butadiene, 686
Bromocyclohexane, preparation of, 769, 770
—, reaction with alkalies, 773
—, — aniline, 772
—, — mercurous fluoride, 773
—, — piperidine, 772, 773
—, — sodium malonate, 773
—, use in Grignard reaction, 771, 772
2-Bromocyclohexanol, preparation of, 531
Bromocyclopentane, preparation of, 764
—, reduction of, 764
—, use in Grignard reaction, 764, 765
1-Bromo-4,4-dimethylpentane, preparation of, 318
1-Bromo-4,4-dimethyl-1-pentene, preparation of, 318
β-Bromoethylarsenic dibromide, preparation of, 527
α-Bromoethylbenzene, formation of, 318
β-Bromoethylbenzene, formation of, 318
Bromoethylethylene, reaction with acetic acid, 313
Bromoform, from acetone, 430
—, catalyst, in cracking, 114
—, structure of, 729
1-Bromohexanol-2, preparation of, 589
1-Bromo-2-iodopropane, preparation of, 317
Bromonaphthalenesulphonic acids, dehydration of tertiary alcohols with, 411
1-Bromonaphthalene-4-sulphonic acid, catalyst, pyrolysis of olefins, 87
Bromopentanes, preparation of, 318, 763
Bromopentene, pentyne from, 514
9-Bromophenanthrene, reaction with magnesium, 824
Bromophenol blue, estimation of acetone, 425
Bromosulphalein test, 1262
Bromotoluenes, from toluene, 795
Bromoundecenoic acids, preparation of, 318
Bromovaleric acids, preparation of, 318
Bromthymol blue, indicator, hydration of propene, 359
Brucite, *see* magnesium hydroxide
Brush discharge, action on benzene, 260
Burning oil, from green oil, 242
Burning point, definition of, 1170
1, 2-Butadiene, *see* Methylallene
1, 3-Butadiene, *see* Butadiene
Butadiene, action of mercury arc on, 265
—, autopolymerization of, 692
—, bromination of, 683-685
—, 1-bromo-2-butene from, 686
—, 2-bromo-2-butene from, 686
—, by cracking cylinder oil, 137
—, — gasoline, 136
—, — kerosene, 144
—, — paraffin wax, 138
—, by dehydration of 1, 3-butene glycol, 174
—, by dehydrogenation of butene, 186
—, by electrical decomposition of ethylene, 258
—, — hydrocarbons, 253, 255
. by oxidation of 2-butene, 897
—, by polymerization of cracking gases, 645, 646
—, — ethylene, 637
—, by pyrolysis of alcohols, 673
—, — 2-butene, 83, 172
—, — by-products of Lebedev process, 173
—, — cyclohexane, 92, 93, 136, 185
—, — cyclohexane homologues, 171, 172

Butadiene, by pyrolysis of cyclohexene, 93
—, — decalin, 93
—, — dichlorobutanes, 678
—, — ethyl alcohol, 173, 177, 347, 676
—, — ethylcyclohexane, 93
—, — ethylene, 78, 172
—, — hydrocarbons, 673, 676
—, — isobutene, 86
—, — methylallene, 88
—, — methylcyclohexane, 93
—, — natural gas, 171, 172
—, — propane, 61, 172
—, — propene, 81
—, by reduction of diacetylene, 677, 678
—, chlorination of, 685
—, condensation with aryl amines, 691
—, — maleic acid, 945
—, — α-naphthoquinone, 175
—, 1,4-dibromobutane from, 684, 685
—, 1, 2-dichlorobutene from, 685
—, 1, 4-dithiocyanobutene from, 698
—, estimation of, 173, 698-700, 1147
—, estimation of acetylene in, 701
—, from butene-2-dichloride, 510
—, from *n*-butyl chloride, 678
—, from cracking gases, 389
—, from dibromocyclobutane, 763
—, from 1,2,3,4-tetrachlorobutane, 807
—, halogenated ethers from, 698
—, hydrogenation of, 699
—, octane number of, 1028
—, polymerization of, 57, 265, 387, 389, 650-652, 673, 674, 1116
—, reaction with alkoxyalkyl halides, 698
—, — benzoquinone, 699
—, — bromine, 683-685
—, — cyclohexene, 186
—, — ethylene, 186
—, — hydrobromic acid, 699
—, — hydrogen bromide, 686
—, — hydrogen chloride, 686
—, — iodosilver benzoate, 697
—, — lithium and ethylaniline, 698
—, — maleic anhydride, 698, 699
—, — methoxy benzylchloride, 698
—, — quinones, 699
—, — thiocyanogen, 698
—, removal from cracking gases, 651, 652
—, — hydrocarbon gases, 673
—, — products of pyrolysis, 174-176
—, separation from acetaldehyde, 175
—, solubility in cuprous salt solutions, 175
—, stability of, 677
—, synthetic rubber from, 173, 177, 672-674
—, tetrachlorobutadiene from, 685
Butadiene compounds, reaction with hydrogen chloride, 686
Butadiene homologues, reaction with sulphur dioxide, 694-696
Butadiene sulphones, bromination of, 694
—, hydroxysulphones from, 695, 696
—, preparation of, 694-696
—, structure of, 695, 696
Butane, acetaldehyde from, 863
—, acetic acid from, 859,
—, acetone from, 863
—, acetylene from, 168
—, alcohols from, 859
—, aromatics from, 181, 190
—, as anesthetic, 1256
—, as dielectric, 728
—, as extraction agent, 972
—, as motor fuel, 26, 1040
—, by pyrolysis of hexadecane, 202
—, — *n*-hexane, 71
—, carbon black from, 219
—, chlorination of, 751, 752
—, combustion of, 1003, 1004
—, commercial, specifications, 25
—, formic acid from, 859
—, from gasoline, 24
—, from methyl ethyl ketone, 449
—, heat of combustion, 15
Butane, hydrogen from, 275
—, ignition temperature of, 992
—, inflammability limits of, 980, 984
—, methyl alcohol from, 863
—, olefins from, 63, 160
—, oxidation of, 852, 859, 863
—, —, effect of hydrogen and carbon monoxide, 869
—, pyrolysis of, 62, 160, 161, 241
—, reaction with nitrosyl chloride, 1101
—, — steam, 275, 280
—, utilization of, 25, 26, 27
n-Butane, acetylene from, 64, 166
—, action of aluminum chloride on, 200
—, 1-butene from, 63, 153
—, —, free energy change, 1284
—, chlorination of, 752
—, cracking, effect of ethylene oxide on, 555
—, —, — hydrogen chloride on, 200, 201
—, effect on viscosity of crystal oil, 15
—, ethane from, 62, 64, 201
—, ethylene from, 62-64
—, from natural gas, 22
—, from petroleum gas, 21
—, hydrogen from, 62
—, isomerization to isobutane, 201
—, —, entropy change, 1282
—, —, free energy change, 1282
—, —, heat of reaction, 1282
—, methane from, 62, 201
—, oxidation of, 874
—, propane from, 201
—, propene from, 62, 64
—, pyrolysis of, 52, 61-64, 150, 152
—, reaction with carbon monoxide, 1099, 1100
1, 2-Butanediol, *see* 1,2-Butene glycol
2, 3-Butanediol, *see* 2,3-Butene glycol
Butanes, azeotropic mixtures with, sulphur dioxide, 1141
—, nitration of, 1087
Butanol, *see* Butyl alcohol
1-Butanol, *see* *n*-Butyl alcohol
2-Butanol, *see* *sec*-Butyl alcohol
Butanolamines, as extraction agents for acids, 590
—, — for ethylene, 164
—, properties of, 588
2-Butanone, *see* Methyl ethyl ketone
Butene, as motor fuel, 1040
—, butadiene from, 186
—, by polymerization of ethylene, 636, 639
—, — propene, 641
—, by pyrolysis of *n*-butane, 153
—, — nonene, 72
—, — propene, 75
—, chlorohydrin from, 518
—, dibutyl sulphate from, 392
—, estimation in cracked gases, 1142
—, in commercial butane, 25
—, reaction with methyl alcohol, 606, 607
—, — sulphuric acid, 385-387
—, removal with carbon, 165
—, — cuprous chloride, 175
n-Butene, *sec*-butyl alcohol from, 387
—, by cracking gas oil, 140
—, by pyrolysis of *n*-butane, 63
—, effect on polymerization of propene, 642
—, polymerization of, 386, 642
—, — with butadiene, 387
1-Butene, bromination of, 510
—, *sec*-butyl alcohol from, 386
—, by dehydration of *sec*-butyl alcohol, 400
—, by dehydrogenation of *n*-butane, free energy change, 1284
—, by polymerization of ethylene, 258
—, by pyrolysis of neopentane, 69
—, — *n*-pentane, 68
—, — 1-pentene, 86
—, — 2-pentene, 86
—, chlorination of, 508
—, hydration of, 293
—, hydrogen from, 83
—, isobutene from, 83
—, isomerization of, 81
—, polymerization of, 81, 642

1-Butene, pyrolysis of, 81, 83
—, reaction with acetyl chloride, 612
—, — benzene, 591
—, — hydrogen bromide, 317
—, — sulphuric acid, 308, 309
2-Butene, butadiene from, 83, 172
—, butene chlorohydrin from, 519, 520, 547, 548
—, *dl*-2-butene glycol from, 547, 548
—, *meso*-2-butene glycol from, 547, 548
—, *sec*-butyl alcohol from, 293, 386, 389
—, by dehydration of *sec*-butyl alcohol, 173, 400
—, by pyrolysis of isopentane, 69
—, — 1-pentene, 86
—, — 2-pentene, 86
—, chlorination of, 172, 508
—, 3-chloro-2-butanol ethers from, 627
—, desorption from silica gel, 165
—, 1,2-dimethyl-1,3-propanediol from, 624
—, hydration of, 293
—, isomerization of, 81, 82
—, molal entropy of, 1291
—, oxidation of, 588, 897
—, polymerization of, 81, 641, 642, 895
—, pyrolysis of, 83, 172
—, reaction with acetic acid, 313
—, — acetyl chloride, 612
—, — alkyl hypochlorites, 627
—, — carbon monoxide, 626
—, — formaldehyde and acetic acid, 624
—, — hypochlorous acid, 509, 547, 548
—, — nitrogen pentoxide, 621
—, — sulphuric acid, 308, 309
—, removal with cuprous chloride, 175
—, — silica gel, 165
—, steric modifications of, 82
—, trimethylacetic acid from, 626
Butene chlorohydrin, butene oxide from, 548
—, from butene, 518
—, from butene-2, 509, 547, 548
—, reaction with potassium hydroxide, 548
Butene dibromides, reaction with potassium iodide, 1146, 1147
Butene dichloride, from butene, 508, 509
Butene dinitrite, from 2-methylpropene, 622
Butene glycols, properties of, 547
Butene oxide, from butene chlorohydrin, 548
—, reaction with aromatic amines, 587
—, — calcium oxide, 590
—, — cellulose esters, 590
1-Butene dibromide, ethyl propiolic acid from, 511
1-Butene di-iodide, preparation of, 511
1-Butene nitrosite, preparation of, 620
1-Butene oxide, from 1-chloro-2-butanol, 589
1, 2-Butene glycol, oxidation of, 549
1, 3-Butene glycol, butadiene from, 174
—, from acetaldol, 547
2-Butene chlorohydrin, from 2-butene, 519, 520
—, ethers from, 520
2-Butene dichloride, as solvent, 510
—, butadiene from, 510
2-Butene oxide, isomerization of, 588
—, preparation of, 588
—, reaction with diethylmagnesium, 588
2, 3-Butene glycol, adlehydes from, 536
—, biacetyl from, 548
—, from 2-butene, 547, 548
—, from sucrose, 547
—, oxidation of, 536
Butenes, *n*-butyl alcohol from, 293
—, *sec*-butyl alcohol from, 294
—, estimation of, 1146, 1147
—, from cracking gas, 144
—, hydration of, 293-296
—, —, heat of, 294
—, isomerization of, 642
—, methyl ethyl ketone from, 293
—, polymerization of, 641, 642, 643
—, reaction with sulphuric acid, 389-391
n-Butenes, cyclohexadiene from, 81
—, cyclohexane from, 81
—, dibutyl sulphate from, 309
—, methylcyclohexadiene from, 81
—, pyrolysis of, 81-83
n-Butenes, reaction with acetic acid, 312, 314
—, — sulphuric acid, 309
—, removal with cuprous chloride, 359
Butenyne, by pyrolysis of acetylene, 89
Butter fat, stabilizer, for ether, 336
Butter substitute, biacetyl in, 708
Butyl acetate, from acetaldehyde, 340
—, from *n*-butenes, 314
—, from ethyl alcohol, 338
—, in rubber cement, 374
n-Butyl acetate, as cleaning agent, 408
—, narcotic properties of, 405
sec-Butyl acetate, as dewaxing agent, 373, 408
—, as solvent for lacquers, 408
—, as thinning agent for lacquers, 408
sec-Butyl acetate, from 2-butene, 313
—, from butyl alcohol, 408
—, from olefins, 298
—, separation of, 408
ter-Butyl acetate, from *ter*-butyl alcohol, 412, 438
ter-Butylacetic acid, by oxidation of diisobutylene, 895
Butylacetylene, oxidation of, 903
—, preparation of, 722
—, reaction with mannitol, 724
—, valeric acid from, 903
ter-Butyl acid sulphate, hydrolysis of, 394
Butyl alcohol, as antiknock, 1017
—, as dewaxing agent, 728
—, as extraction agent for oils, 1200
—, — for α-polyprene, 681
—, butyraldehyde from, 878, 880
—, esters from, 339
—, from acetaldehyde, 340
—, from crotonaldehyde, 889
—, from ethyl alcohol, 173, 339-341
—, from petroleum ether, 853
—, in anti-rust compositions, 577
—, in rubber cement, 374
—, oxidation of, 880
—, reaction with acetone, 443
—, — phthalic anhydride, 501
n-Butyl alcohol, as blending agent for fuel, 1035
—, from butenes, 293
—, from butyl chloride, 797
—, from ethyl alcohol, 337
—, in gasoline mixtures, 375
—, octane number of, 1028
sec-Butyl alcohol, as extraction agent for sulphonates, 373
—, as homogenizing agent for nitrocellulose composition, 406
—, azeotropic mixture with water, 407, 408
—, 2-butene from, 173
—, dehydration of, 400
—, esterification of, 1081
—, from *n*-butene, 387
—, from butene-1, 386
—, from butene-2, 293, 386, 389
—, from butenes, 294
—, from olefins, 404
—, propionic acid from, 407
—, pyrolysis of, 173
—, reaction with aromatics, 402
—, — carbon monoxide, 407
—, — lactic acid, 405
—, — resorcinol, 403
—, removal with petroleum ether, 407
—, solubility in water, 404
ter-Butyl alcohol, acetylation of, 438
—, as dewaxing agent, 414, 415
—, as extraction agent for asphalt, 414, 415
—, as fuel, 417
—, chlorohydrin from, 518
—, drying with phthalic anhydride, 417
—, estimation, in isopropyl alcohol, 365, 371, 372
—, from *ter*-butyl chloride, 798, 799
—, from cracked gasoline, 389
—, from isobutene, 386, 390, 391
—, —, free energy change, 1303
—, in gasoline mixtures, 375, 417
—, in molecular weight determination, 415, 416
—, pyrolysis of, 410

ter-Butyl alcohol, reaction with acetic acid, 412
—, — acetyl chloride, 412
—, — benzene, 411
—, — chlorine and cinnamic acid, 627
—, — cresols, 412, 416
—, — cymene, 412, 416
—, — hydrochloric acid, 417
—, — isopropylbenzene, 412
—, — mercuric sulphate, 365
—, — phenol, 412, 416
—, — sodium, 418
—, — sulphuric acid, 365, 417
—, *see also* 2-Methyl-2-propanol
—, *see also* Trimethylcarbinol
—, stability of hydrogen peroxide in, 895
Butylbenzene, naphthalene from, 74
n-Butylbenzene, action of aluminum chloride on, 208
—, benzene from, 208
—, dibutylbenzene from, 208
—, in gasoline, 144
sec-Butylbenzene, from benzene, 402
—, in gasoline, 144
ter-Butylbenzene, from benzene, 411, 592
—, from petroleum, 35
—, molal entropy of, 1289
Butyl bromide, reaction with calcium acetylide, 722
n-Butyl bromide, *see* 1-Bromobutane
sec-Butyl bromide, *see* 2-Bromobutane
ter-Butyl bromide, from isobutene, 317
—, hydrolysis of, 800
2-*ter*-Butylbutadiene, preparation of, 678
Butylcellulose, preparation of, 753
Butyl chloride, from cracking gas, 302
—, reaction with magnesium, 823
n-Butyl chloride, butadiene from, 678
—, chlorination of, 678
—, hydrolysis of, 797
—, *see also* 1-Chlorobutane
sec-Butyl chloride, *see* 2-Chlorobutane
ter-Butyl chloride, chlorination of, 752
—, dechlorination of, 806
—, from *ter*-butylethyl ether, 414
—, from isobutyl chloride, 752
ter-Butyl chloride, hydrolysis of, 412, 798, 799
—, reaction with phenol, 418, 818
—, *see also* 2-Chloro-2-methylpropane
Butyl chlorosulphites, preparation of, 413
Butylcresol, as extraction agent for isopropyl alcohol, 360
o-*ter*-Butyl-*m*-cresol, preparation of, 412, 416
Butylcyclopentane, pyrolysis of, 91
Butylcyclopentyl carbinol, preparation of, 765
ter-Butylcymene, preparation of, 416
Butyl ether, peroxides from, 336
ter-Butylethylene, polymerization of, 643, 645
—, preparation of, 87, 411, 645
—, tetramethylethylene from, 87
ter-Butylethyl ether, reaction with hydrogen chloride, 414
—, preparation of, 753
Butyl formate, as insecticide, 408, 409
ter-Butyl hypochlorite, absorbent for ethylene, 627
—, preparation, 518
—, reaction with olefins, 518
Butyl iodide, reaction with mercurous fluoride, 753
ter-Butyl isocyanide, effect on propene-hydrogen bromide reaction, 316
Butyl lactate, hydrogenation of, 546
—, propene glycol from, 546
sec-Butyl lactate, preparation of, 405, 409
Butyl mercaptan, as stabilizing agent, 730
—, estimation of sulphur, 1156, 1157
ter-Butyl mercaptan, from isobutene, 463
ter-Butylmethyl carbinol, *see* 3,3-Dimethyl-2-butanol
ter-Butylmethylethylene, trimethylethylethylene from, 87
Butyl oxalate, as antiknock, 1017
Butyl oxide, as stabilizing agent, 743
p-*sec*-Butylphenol, from *sec*-butylphenyl ether, 403
ter-Butylphenol, preparation of, 403, 412, 818
o-*ter*-Butylphenol, preparation of, 418
p-*ter*-Butylphenol, preparation of, 403, 418
ter-Butylphenols, utilization of, 818
Butylphenyl ethers, isomerization of, 403
Butyl phthalate, as antiknock, 1017
—, preparation of, 501
N-Butylpiperidines, preparation of, 773
Butyl propionate, from acetaldehyde, 340
ter-Butyl-*sec*-propyl ether, preparation of, 414
n-Butylsulphonic acid, butyric acid from, 1067
ter-Butylsulphuric acid, from isobutene, 308
ter-Butyltoluene, preparation of, 411
p-*ter*-Butyltoluene, reaction with isopropyl chloride, 816
1-Butyne, preparation of, 722
Butyraldehyde, condensation of, 889
—, from butyl alcohol, 878, 880
—, from crotonaldehyde, 889
—, iso-octenyl aldehyde from, 878
—, octyl alcohol from, 889
—, ozonization of, 887
Butyric acid, dipropyl ketone from, 443
—, from *n*-butylsulphonic acid, 1067
—, from carbohydrates, 443
—, from carbon monoxide and hydrogen, 1244
—, from cracked gasoline, 854
—, from paraffin wax, 971
—, solvent for ketene, 437
Butyrolactone, as extraction agent for acetylene, 169

C

Cadmium, catalyst, polymerization of olefins, 665
—, —, pyrolysis of methane, 55
—, —, — olefins, 78
—, —, — paraffins, 159
—, —, reaction of acetylene and amines, 719
—, reaction with trichloroethylene, 711
—, stabilizing agent for ethylene oxide, 554
Cadmium acetate, catalyst, acetylene-acetic acid reaction, 717
Cadmium antimonide, catalyst, dehydrogenation of alcohols, 419
Cadmium arsenide, catalyst, dehydrogenation of alcohols, 419
Cadmium bismuthate, catalyst, dehydrogenation of alcohols, 419
Cadmium bromide, catalyst, propene-acetic acid reaction, 308
Cadmium chloride, catalyst, propene-acetic acid reaction, 308
—, in preparation of 2,3-dialkyldioxanes, 581
Cadmium chromite, catalyst, dehydrogenation of alcohols, 420
Cadmium discresyl, antioxidant for lubricants, 938
Cadmium halides, catalysts, dehydrogenation of hydrocarbons, 158
—, —, fluorination of dichloroethane, 747
—, —, hydration of acetylene, 712
—, —, reaction of olefins and carbon monoxide, 625, 626
Cadmium oxide, catalyst, ethanol-steam reaction, 422
—, —, decarboxylation of phthalic anhydride, 951
—, —, hydration of ethylene, 291
—, —, oxidation of acenaphthene, 946
—, —, — aromatics, 942
—, —, — naphthalene, 946
—, effect on ignition temperatures, 1000
Cadmium phosphate, catalyst, hydration of ethylene, 287, 288, 290
—, —, hydration of propene, 293
—, —, polymerization of olefins, 634
—, —, reaction of ethers and alkyl halides, 345
—, —, — propene and acetic acid, 308
Cadmium phosphide, catalyst, dehydrogenation of secondary alcohols, 419
Cadmium salts, catalysts, hydration of vinylacetylene, 705
—, —, polymerization of olefins, 929
—, —, reaction of acetylene and phenol, 715
—, —, — ethylacetylene and acetic acid, 718
Cadmium selenide, catalyst, dehydrogenation of alcohols, 419

Cadmium sulphate, catalyst, propene-acetic acid reaction, 308
—, —, hydration of ethylene, 283
—, reaction with triethanolamine, 571
Cadmium sulphide, catalyst, pyrolysis of mercaptans, 472, 479
Cadmium telluride, catalyst, dehydrogenation of alcohols, 419
Caesium carbonate, catalyst, condensation of alcohols, 340
Caffeine, extraction with dichloroethane, 745
—, stabilizing agent for tetrachloroethane, 743
Calcium, catalyst, ethers from acetals, 715
—, —, oxidation of paraffins, 874
—, desulphurizing agent, 489
Calcium acetylide, preparation of, 722
—, reaction with diethyl sulphate, 722
Calcium alkylsulphonates, surface tension of, 1066, 1067
Calcium antimonide, catalyst, dehydrogenation of alcohols, 419
Calcium arsenide, catalyst, dehydrogenation of alcohols, 419
Calcium bismuthate, catalyst, dehydrogenation of alcohols, 419
Calcium bisulphide, reaction with vinyl sulphone, 618
Calcium borate, catalyst, ethanol-steam reaction, 422
Calcium boro-phosphate, catalyst, hydration of butenes, 294
—, —, — ethylene, 285
—, —, — propene, 292
Calcium bromide, reaction with diethanolamine, 572
—, — triethanolamine, 572
Calcium butyrate, preparation of, 443
Calcium carbide, reaction with deuterium oxide, 743
Calcium carbonate, catalyst, acetone from ethyl alcohol, 423
—, —, chlorination of trimethylethylene, 513
—, —, cracking of wax acids, 979
—, —, ethanol-steam reaction, 422
—, —, hydration of ethylene, 291
—, —, oxidation of ethyl alcohol, 423
—, —, polymerization of ethylene oxide, 562
—, —, pyrolysis of methane, 218, 227
—, reaction with ethylene dichloride, 533
Calcium caseinate, in insecticides, 1112
Calcium chloride, catalyst, acetylene-hydrogen chloride reaction, 716
—, —, chlorination of propene dichloride, 507
—, —, dechlorination of propyl chloride, 806
—, —, propene-hydrogen chloride reaction, 306
—, dehydration agent for *sec*-butyl alcohol, 404
—, — isopropyl alcohol, 364
—, demulsifying agent, 1105
—, extraction agent for amylene, 173
—, — piperylene, 173
—, in fermentation of sucrose, 547
—, in gas analysis, 1123
—, in purification of napthenic acids, 1109
—, promoter, reduction of carbon monoxide, 1229
—, reaction with isopropyl alcohol, 370
—, — methane, 1102
—, — triethanolamine, 572
—, removal of acetylene with, 170
—, stabilizing agent for asphalt emulsions, 1215, 1218
Calcium compounds, catalysts, acetylene-steam reaction, 714
Calcium dihydrogen phosphate, catalyst, oxidation of ethylene, 894
Calcium fluoride, reaction with carbon tetrachloride, 736, 737
—, — chloroform and silver fluoride, 737
Calcium halides, catalysts, hydration of acetylene, 712
Calcium hydride, catalyst, in cracking, 115
Calcium hydroxide, catalyst, acetone from acetic acid, 423
—, —, chlorination of propene dichloride, 507
—, —, decarboxylation of phthalic anhydride, 950
—, —, hydrolysis of methyl chloride, 796
Calcium hydroxide, dehydration agent for isopropyl alcohol, 365
—, extraction agent for naphthenic acids, 1107
—, — wax acids, 976
Calcium hypochlorite, reaction with diethyl ketone, 453
—, separation of acids with, 968
Calcium iodide, reaction with triethanolamine, 572
Calcium monophosphate, catalyst, reaction of olefins and carbon monoxide, 626
Calcium naphthenate, antioxidant for lubricants, 937
—, catalyst, oxidation of paraffin wax, 971
—, —, — petroleum, 963, 972
—, in inks, 1117
Calcium nitrate, solubility in isopropyl alcohol, 370, 375
Calcium oxide, catalyst, acetone from acetic acid, 423
—, —, chlorination of propene dichloride, 507
—, —, condensation of acetone, 429
—, —, decarboxylation of phthalic anhydride, 950, 951
—, —, dipropyl ketone from *n*-butyl alcohol, 443
—, —, ethylene oxide from ethyl hypochlorite, 551
—, —, in cracking, 128, 137
—, —, oxidation of ethyl alcohol, 423
—, —, polymerization of ethylene oxide, 562
—, —, pyrolysis of oxygenated hydrocarbons, 340
—, —, wax acid-pentaerythritol reaction, 1055
—, dehydration agent for isopropyl alcohol, 364
—, extraction agent for naphthenic acids, 1105
—, in preparation of morpholine, 583
—, promoter, dechlorination of butyl chloride, 806
—, —, in cracking, 112
—, —, methane-steam reaction, 272
—, —, reduction of carbon monoxide, 1240
—, reaction with butene oxide, 590
—, — trichloroacetaldehyde and deuterium oxide, 729
—, refining agent for gasoline, 669
—, solubility in isopropyl alcohol, 375
Calcium phosphate, catalyst, dechlorination of propyl chloride, 805
—, —, ethanol-steam reaction, 422
—, —, hydration of ethylene, 287
—, —, — propene, 292
Calcium phosphides, catalysts, dehydrogenation of alcohols, 419
Calcium rosinate, stabilization of asphalt emulsions, 1217
Calcium selenide, catalyst, dehydrogenation of alcohols, 419
Calcium silicate, catalyst, ethanol-steam reaction, 422
—, —, oxidation of ethanol, 423
Calcium soaps, catalysts, oxidation of paraffin wax, 972
—, in grease, 1079
—, in lubricants, 1079
Calcium sucrate, antioxidant for gasoline, 917
Calcium sulphate, catalyst, ethylene-sulphuric acid reaction, 323
—, —, hydration of propene, 292
—, —, sulphation of propene, 358
Calcium sulphide, reaction with ethylene dichloride, 499
Calcium sulphocyanide, catalyst, esterification of cellulose, 588
Calcium sulphonates, as emulsifying agents, 1074
—, extraction of, 1065
—, in insecticides, 1077, 1078
Calcium telluride, catalyst, dehydrogenation of alcohols, 419
Camphor, antioxidant for gasoline, 918
—, as antiknock, 1017
—, from borneol, 444
—, in motor fuel, 1039
—, in polyprene, 681
—, preparation of, 688
—, reaction with nitric acid, 851, 852
Camphoric acid, antioxidant for gasoline, 918
Camphorone, antioxidant for gasoline, 918
Candle wax, preparation of, 543

Candles, Kogasin in, 1255
—, paraffin wax in, 1255
Caproic acid, formation of, 904
Capryl alcohol, *see* 2-Octanol
Carbazole, alkylation of, 595
Carbenes, action of carbon tetrachloride on, 1196
—, by polymerization of acetylene, 704
—, by pyrolysis of naphthenes, 196
—, definition of, 1193
—, estimation of, 1193
—, from lubricating oil, 855, 932
—, in asphalts, 1193
—, reaction with sulphuric acid, 1193
Carbides, catalysts, oxidation of paraffin wax, 971
Carbitol, in brake fluid mixtures, 578
Carboids, by hydrogenation of shale tar, 1194
—, by oxidation of asphaltenes, 1203
—, estimation of, 1193
—, reaction with sulphuric acid, 1193, 1194
Carbon, adsorption of alcohols, 1075
—, — butadiene, 174
—, — ethylene, 324
—, — naphthenes, 1149, 1150
—, — olefins, 328
—, — paraffins, 1149, 1150
—, — saponifiable acids, 732
—, — saponifiable oils, 732
Carbon, by cracking kerosene, 137
—, — sapropelites, 143
—, — *n*-tetradecane, 1297
—, by electrical decomposition of methane, 253
—, by pyrolysis of benzene, 191
—, — *n*-butane, 64
—, — ethane, 56, 151
—, — *n*-hexane, 71
—, — isobutene, 85
—, — methane, 54, 218-220
—, — natural gas, 220, 228
—, — paraffins, 159, 188
—, — 2-pentene, 87
—, — propane, 61
—, carbon tetrachloride from, 730
—, catalyst, acetic acid from ethyl chloride, 830
—, —, acetylene-hydrogen chloride reaction, 716
—, —, carboxylic acids from olefins, 446
—, —, chlorination of methane, 726
—, —, chlorination of toluene, 793
—, —, condensation of carbon tetrachloride, 731
—, —, dechlorination of tetrachloroethane, 805
—, —, ethanol-steam reaction, 422
—, —, for fluorination, 735, 736
—, —, in cracking, 111, 137
—, —, ketene-hydrogen chloride reaction, 439
—, —, methane-steam reaction, 278
—, —, oxidation of ethylene, 894
—, —, oxidation of petroleum, 964
—, —, polymerization of olefins, 636
—, —, pyrolysis of acetylene, 89
—, —, — benzene, 192
—, —, — hydrocarbons, 158
—, —, — olefins, 158
—, —, — propane, 189
—, coagulation, by sulphonic acids, 1081
—, desulphurizing agent, 1043
—, effect on pyrolysis of 2-butene, 172
—, from petroleum coke, 231
—, in lubricants, 930, 931
—, in purification of phthalic anhydride, 961
—, methane from, 1278
—, promoter, oxidation of toluene, 950
—, —, reaction of benzene and chlorine, 778
—, —, reduction of carbon monoxide, 1228
—, reaction with hydrogen, 168, 1278
—, — methane, 168
—, — sulphur dichloride, 730
Carbonating muds, as emulsifying agents, 1217
Carbon black, absorption of oil, 246
—, adsorptive power, determination, 249, 252
—, —, effect on rubber on, 252
—, ash in, 251
—, color index of, 248
—, color intensity, 246
—, —, effect of compression, 246
—, —, effect of vibration, 246
—, color measurement of, 252
Carbon black, combustion of, 245
—, dispersion of, 248, 1117
—, effect of channel height on, 239
—, — flame structure on, 239
—, effect on curing of rubber, 249
—, electrostatic precipitation of, 222
—, extraction with acetone, 251
—, extraction with benzene, 251
—, from acetylene, 223, 235, 242
—, from butane, 219, 237
—, from carbon monoxide, 229
—, from ethane, 240
—, from gaseous hydrocarbons, 224, 235, 237
—, from gilsonite, 244
—, from methane, 219, 236, 240, 255
—, from natural gas, 23, 220, 222, 236
—, from olefins, 237
—, from petroleum oils, 226, 255
—, from propane, 219, 237, 240
—, from resin, 244
—, from still residues, 244
—, ignition temperature of, 245
—, in clarifying wine, 232
—, in nitrocellulose lacquer, 247
—, in printing ink, 250
—, in rubber, 240, 245, 246, 249, 250
—, oil-absorption index, 248
—, particle size, 249
—, utilization of, 249, 250, 251
—, wetting of, 246
—, X-ray diffraction patterns, 245
Carbon dioxide, carbon monoxide from, 1247
—, deasphalting agent, 45
—, effect on absorptive power of carbon black, 249
—, — acetylene polymerization, 267
—, — combustion, 1004
—, — decomposition of ethylene oxide, 554
—, — gasoline, 924
—, — ignition temperature, 998
—, — inflammability limits, 983, 984, 985
—, — Kogasin synthesis, 1235, 1241, 1242
—, — methane oxidation, 264
—, — osmotic resistance of erythrocytes, 1261
—, — stability of methyl nitrate, 1093
—, estimation in ethylene, 1259, 1260
—, — natural gas, 1123
—, ethylene from, 1241
—, extraction of ethylenediamine with, 497
—, from benzene, 273
—, from carbon monoxide, 277, 278
—, from carbon tetrachloride, 731
—, from cyclohexane, 273
—, from cyclohexene, 273
—, from ethyl acetate, 421
—, from ethyl alcohol, 348, 351, 353
—, from ethylene, 551, 552, 897
—, from hexane, 273
—, from hydrocarbon oils, 131
—, from hydrocarbons, 269
—, from isopropyl alcohol, 371
—, from methane and steam, 270-273
—, from 2-methyl-propene, 622
—, from natural gas, 22, 1121
—, from phenylacetylene, 904
—, from *m*-xylene, 273
—, in crude oil, 10
—, in fumigants, 556
—, methane from, 1241, 1242
—, pressure-volume-temperature relations, 1321, 1322
—, reaction with benzene, 260
—, — coke, 1247
—, — ethylene bromohydrin, 532
—, — ethylene chlorohydrin, 532
—, — ethylene dibromide, 532
—, — ethylene dichloride, 532
—, — dihydronaphthalene, 958
—, — hydrogen, 661
—, — methane, 273-275, 870, 1246
—, — natural gas, 278
—, — phthalic anhydride, 950
—, reduction of, 1247
—, removal with ethanolamines, 574

Carbon disulphide, carbon tetrachloride from, 730
—, catalyst, in cracking, 112
—, —, reaction of ethylene dichloride and sodium polysulphide, 499
—, combustion of, 1003, 1004
—, effect on Kogasin synthesis, 1236
—, from acetylene, 467, 720
—, from carbon tetrachloride, 469
—, from mineral oil, 468
—, ignition temperature of, 987
—, inflammability limits of, 980
—, inhibitor, deposition of carbon, 192
—, oxidation of, 851
—, peptizing agent for asphalts, 1196
—, promoter, reaction of propyl benzene and propionyl chloride, 447
—, reaction with chlorine, 730
—, — hydrogen fluoride and chlorine, 737
—, — nitroparaffins, 1096
—, solvent, asphalt components, 1190, 1193, 1200
Carbonic acid, reaction with hydroxyalkylamines, 569
Carbonit earth, use in refining lignite spirits, 928
Carbon monoxide, acids from, 1223, 1244, 1245
—, alcohols from, 1049, 1223, 1244, 1251, 1252
—, —, free energy change, 1303-1305
—, aldehydes from, 1223, 1244
—, aromatics from, 1243
—, carbon black from, 229
—, catalyst, polymerization of olefins, 636
—, combustion of, 1010
—, Diesel fuel from, 1250
—, effect on chlorination of olefins, 493
—, — decomposition of acetaldehyde, 884
—, — decomposition of ethylene oxide, 554
—, esters from, 1223
—, estimation in ethylene, 1259, 1260
—, estimation in gaseous hydrocarbons, 1124, 1127, 1128, 1133
—, free energy of formation, temperature effect, 1304
—, from butane, 275
—, from carbon dioxide, 274, 1247
—, from coal, 1246
—, from coke, 1247
—, from coke-oven gas, 1246-1248
—, from ethyl alcohol, 347-349, 352, 353
—, from ethylene, 622
—, from ethylene oxide, 554
—, from generator gas, 1246
—, from hydrocarbons, 269
—, from kerosene, 272
—, from ketene, 437
—, from methane, 224, 226, 270 274, 1246
—, from methyl ethyl ketone, 449, 450
—, from petroleum, 17
—, from petroleum gases, 21, 1048
—, from propane, 275
—, from still gases and steam, 229
—, from water, 256
—, from water gas, 1246
—, Gasol from, 1250
—, gasoline from, 1229, 1231, 1235, 1243, 1245, 1247, 1250-1252
—, ignition, 1001
—, —, effect of nitrogen on, 1001, 1002
—, ignition temperature of, 987, 988, 997
—, inflammability limits of, 985
—, ketones from, 1223, 1244
—, Kogasin from, 1223
—, lamp oil from, 1250
—, olefins from, 1223, 1235, 1241-1243
—, oxidation of, effect of temperature on, 850
—, paraffins from, 1223, 1226, 1235, 1236, 1240 1243, 1245, 1250
—, γ-pyrone from, 1244
—, reaction with alcohols, 407, 1041, 1050
—, — aromatics, 949, 957, 1099
—, — hydrogen, 660, 661
—, —, effect of catalysts, 1228-1230
—, —, mechanism, 1224, 1225
—, —, thermodynamics of, 1225-1227
—, — methyl chloride, 727
—, — olefins, 446, 625, 626, 893
—, — paraffins, 1099
Carbon monoxide, reaction with phthalic anhydride, 950
—, — sodium phenolate, 957
—, — steam, 269, 270, 277, 446, 871
—, reduction of, free energy change, 1303-1305
—, removal with cuprous formate solutions, 234
—, — cuprous lactate solutions, 234
—, Synthin from, 1223
—, Synthol from, 1223
—, terpenes from, 1244
—, use in cracking, 115
—, — oxidation of gaseous hydrocarbons, 851, 893
—, — pyrolysis of hydrocarbons, 156
Carbon remover, preparation of, 486
Carbon silicide, use in pyrolysis of methane, 892
Carbon tetrachloride, action on carbenes, 1196
—, adsorption by carbon, 252
—, as heat transfer medium, 510, 949
—, as parasiticide, 733
—, as solvent, 307, 505, 742
—, carbon dioxide from, 731
—, catalyst, in cracking, 114
—, —, oxidation of ethylene, 894
—, —, polymerization of unsaturates, 214
—, chloral from, 731
—, chloro-fluoromethanes from, 736, 737
—, crystalline forms of, 730
—, decarbonizing with, 731
—, decomposition of, 730
—, dehydration agent for alcohols, 407
—, dewaxing agent for oils, 731
—, dichlorodifluoromethane from, 733, 734
—, effect on decomposition of acetone, 450
—, — esterification of isopropyl alcohol, 376
—, — inflammability limits, 985, 986
—, — pentene-1-hydrogen bromide, reaction, 317
—, electrolysis of, 807
—, estimation of, 729, 731
—, extraction agent for asphaltenes, 1190
—, — naphthenic acids, 1108
—, — polymerized hydrocarbons, 397
—, — trinitrotoluene, 496
—, from carbon disulphide, 730
—, from chlorinated coal, 730
—, from chloromethane, 727
—, from methane, 726
—, from monofluorotrichloromethane, 737
—, from sulphur dichloride and carbon, 730
—, hexachloroethane from, 731
—, inflammability limits of, 980
—, phosgene from, 732, 733
—, phthalyl chloride from, 731, 732
—, precipitant for carbenes, 1193
—, properties of, 730
—, reaction with antimony trifluoride, 733, 734, 736
—, — calcium fluoride, 736, 737
—, — ethers, 345
—, — formaldehyde, 731
—, — petrolatum, 732
—, — phthalic anhydride, 731, 732
—, — sulphur, 469
—, refining agent for oils, 731
—, resin from, 217, 732
—, stabilization of, 733
—, tetrachloroethane from, 731
—, toxicity of, 733
—, trichlorofluoromethane from, 734
—, uses of, 545, 731, 732, 733, 746, 790
Carbonyl compounds, from polyhydric alcohols, 548
Carbonyl fluoride from fluoroform, 737
Carbonyls, as antioxidants for gasoline, 914
—, catalysts, oxidation of paraffin wax, 971
Carboxide, definition of, 556
Carboxylic acids, as extraction agents, 1060
—, catalyst, esterification of olefins, 314, 315
—, extraction with ethers, 418
—, from aldehydes, 885
—, from crude oil, 10
—, from kerosene, 860
—, from ketones, 432, 450
—, from naphthenes, 10
—, from nitrolic acids, 1094

Carboxylic acids, from olefins, 446
—, from paraffin wax, 856
—, from sapropels, 975
—, reaction with vinylacetylene, 706
—, as antioxidant for gasoline, 914
β-*o*-Carboxyphenyl-propionic acid, preparation of, 905
Carburol process, for cracking, 130
Carbyl sulphate, acetic acid from, 1081
—, from ethylene, 321, 1081, 1082
—, isethionic acid from, 1081
Carnauba wax, in polishing compositions, 1079
Caro's acid, hydroxylation of olefins, 532
Casein, in asphalt emulsion, 1219
—, in coating compounds, 1079
—, in insecticides, 1077
—, in synthetic plastics, 890
—, reaction with olefin oxides, 561, 562
Castor oil, as solvent, 1113
—, effect on ignition temperature, 998
—, extraction agent for resins, 1188
—, in brake fluid mixtures, 539, 542, 546
—, in insecticides, 1077
—, oxidized, in demulsifying agents, 1075
—, reaction with naphthenic acids, 1113
—, — resins, 217
—, solubility in di-*n*-propyl ketone, 443
—, — mineral oil, 759
—, sulphonated, in emulsifying agents, 1074
Catalysis, mechanism of, 633, 634
Catalysts, effect, on free energy change, 1296
Catechol, antioxidant for gasoline, 913, 917
—, effect on color stability, 926
Cathode rays, action on gaseous hydrocarbons, 267
Celite earth, catalyst, oxidation of toluene, 949
Celluloid, solvent for, 896
Cellulose, acetylation of, 496
—, etherification of, 559
—, petroleum from, 19
—, reaction with chlorohydrins, 559
—, — ethylene oxide, 558, 559
—, — olefins, 629
Cellulose acetate, plasticizer for, 498
—, solvents for, 415, 434, 443, 453, 582
Cellulose esters, in paints, 1115
—, plasticizers for, 582, 1120
—, reaction with butene oxide, 589
Cellulose ethers, plasticizers for, 1120
Cellulose films, preparation of, 728
Cellulose hydroxypropyl phthalate, preparation of, 588
Cellulose phthalate, reaction with propene oxide, 588
Cellulosic materials, oils from, 21
Cements, formaldehyde in, 890, 891
Ceramics, preparation of, 1057
Ceresin, acids from, 975
—, composition of, 16, 39
—, cracking of, 195
—, definition of, 1245
—, extraction agents for, 1245
—, from crude oils, 13
—, in dielectrics, 1255
—, oxidation of, 975
—, properties of, 39
—, sulphonation of, 39
—, voltolization of, 262
Ceria, catalyst, esterification of alcohols, 338
—, —, pyrolysis of ethylbenzene, 159
Ceric ions, catalysts, nitration of toluene, 954
Cerium, catalyst, chlorination of benzene, 778
—, —, oxidation of ethylene, 553
—, promoter, oxidation of methyl alcohol, 878, 879
—, —, reduction of carbon monoxide, 1229, 1232, 1236, 1240
Cerium acetylacetonates, catalysts, phenylcyclopentane autoxidation, 907
Cerium chloride, promoter, chlorination of methane, 726
Cerium nitrate, catalyst, methane-steam reaction, 278
Cerium oxide, catalyst, hydration of acetylene, 714
—, —, ketones from acids, 446
—, —, oxidation of aromatics, 942
—, —, — hydrocarbons, 850, 851, 871
—, —, reaction of methane and steam, 279
—, —, — nitric oxide and paraffins, 1091
—, promoter, dehydrogenation of isopropyl alcohol, 420
—, —, ethanol-steam reaction, 422
Cerium phosphate, catalyst, dehydration of 1,3-butene glycol, 174
—, —, reaction of ethers and alkylhalides, 345
Cerium sulphate, catalyst, oxidation of anthracene, 954
—, —, — hydrocarbons, 854
Cetane number, definition of, 1034
Cetene, reference standard, in Diesel fuel, 1033, 1034
Cetene number, definition of, 1034
Cetyl acetate, from cetyl alcohol, 438
Cetyl alcohol, acetylation of, 438
—, reaction with olefin oxides, 587, 588
Cetyl halides, glycol ethers from, 543
Chain reactions, in pyrolysis of hydrocarbons, 189
Chamotte, effect on pyrolysis of hydrocarbons, 189
Chancel degrees, definition of, 245
Channel process, for carbon black, 237
Characterization factor, critical temperature from, 1313
—, definition of, 1307
—, determination from aniline point, 1309
—, — hydrogen content, 1309
—, — molal average boiling point, 1307, 1309, 1310
—, — specific gravity, 1307, 1309, 1310
—, — viscosity index, 1309, 1310
—, heat of vaporization from, 1327
—, molecular weight from, 1311
—, of aromatics, 1307
—, of cracked gasoline, 1308
—, of crudes, 1308
—, of paraffins, 1307
—, of residuums, 1308
—, pseudocritical pressure from, 1318, 1319
—, pseudocritical temperature from, 1318, 1319
—, specific heat from, 1323, 1325
Charcoal, adsorption of gaseous hydrocarbons, 164, 1139
—, adsorption of helium, 1125, 1126
—, adsorption of hydrogen sulphide, 461
—, adsorption of liquid hydrocarbons, 23
—, adsorption of mazout, 1188
—, adsorption of resins, 1188
—, catalyst, chlorination of toluene, 793
—, —, dehydrogenation of thiophane, 484
—, —, isomerization of propene oxide, 586
—, —, oxidation of petroleum, 966
—, —, — sodium sulphide, 465
—, —, polymerization of diolefins, 667
—, —, — olefins, 666
—, —, reaction of methane and ammonia, 281
—, —, — methane and carbon oxides, 1049
—, desorption of olefins from, 164
—, in refining isopropyl alcohol, 365
Charging stock, effect on cracking, 107, 108
China wood oil, cracking of, 136
Chloral, from carbon tetrachloride, 731
Chloral deuterate, deuterio-chloroform from, 729
—, reaction with sodium deutroxide, 729
Chlorene, from acetylene, 89, 703
Chlorex, composition of, 43
Chlorex process, refining of oils, 43, 529, 530
Chloric acid, oxidizing agent for mercaptans, 480
ter-Chlorides, hydrolysis of, 413
Chlorinated biphenyls, from monochlorobenzene, 780, 781
Chlorinated hydrocarbons, effect of zinc on, 782
Chlorinated Kogasin, action of aluminum chloride on, 1253, 1254
—, reaction with aromatics, 1253, 1254
Chlorinated naphtha, resins from, 217

Chlorinated paraffins, effect on castor oil solubility, 759
—, in coating compositions, 759
—, in emulsifying agents, 822
—, lubricating oil from, 813
—, olefins from, 807
Chlorinated paraffin wax, lubricants from, 758, 817
—, reaction with benzene, 758
Chlorinated pentane, utilization of, 755
Chlorinated propane, resins from, 217
Chlorinated rubber, in coating compositions, 543
Chlorination, acetone, 430
—, acetylene, 709
—, benzene, 777-781
—, butadiene, 685
—, butane, 751, 752
—, butenes, 172, 508
—, *ter*-butyl alcohol, 627
— *n*-butyl chloride, 678
—, carbon disulphide, 730
—, carbon tetrachloride, 734
—, chloromethane, 727
—, cinnamic acid, 627
—, coal, products from, 730
—, cyclohexane, 765-767
—, cyclohexene, 767
—, cyclopropane, 760, 761
—, of deuterioacetylene, 742, 743
—, dichlorobenzenes, 781
—, difluoromethane, 734, 735
—, dimethyl ether, 529
—, 1,4-dithiocyanobutene, 698
—, divinylacetylene, 709
—, ethane, 741
—, ethyl alcohol, 626, 627
—, ethylene, 492
—, ethylene dichloride, 501, 742
—, formaldehyde, 887
—, gasoline, 755
—, hexane, 756
—, isobutane, 752
—, isobutene, 508
—, isopentadecane, 1253
—, isoprene, 686
—, Kogasin, 1253
—, Kogasin II, 815
—, menthane, 776
—, methane, 726-730
—, methyl alcohol, 626
—, monochlorobenzene, 780, 781
—, naphthenic alcohols, 1120
—, neopentane, 754
—, octane, 756
—, paraffins, rules for, 740
—, paraffin wax, 757
—, pentane, 753, 754
—, pentenes, 511, 512
—, petroleum-coal distillate, 781
—, petroleum distillates, 814
—, polychlorobenzene, 780, 781
—, polyprene, 682
—, propane, 749, 750
—, pyrene, 956
—, still gases, 741
—, tar, 756
—, toluene, 793, 794
—, trimethylcyclohexane, 775, 776
—, trimethylethylene, 513
—, of vinyl chloride, 716
Chlorine, action on hydrogen sulphide, 460
—, catalyst, oxidation of asphalts, 1205
—, —, pyrolysis of paraffins, 158, 168
Chlorine monoxide, chlorination of benzene, 781
Chloroacetaldehyde, from methylene chloride, 728
Chloroacetic acid, catalyst, ethylene oxidation, 894
—, from tetrachloroethane, 746
—, reaction with isopropyl alcohol, 376
—, — propene, 308
4-Chloroacetophenone, from chlorobenzene, 789
β-Chloroacid chlorides, reaction with alcohols, 611
1-Chloro-2-alkoxy-2-phenylpropionic acid, from cinnamic acid, 627
Chloroamine, reaction with ketene, 440
6-Chloro-8-amino-quinoline, reaction with N-aminodiethylethanol, 569
Chloroaniline, as refining agent, 46
Chlorobenzene, *p*-aminobiphenyl from, 787
—, aniline from, 786, 787
—, chlorinated biphenyl from, 780, 781
—, chlorination of, 780, 781
—, 4-chloroacetophenone from, 789
—, *p*-chlorobenzylbenzoic acid from, 789
—, dewaxing agent, 434
—, diphenylamine from, 787
—, diphenyl ether from, 788, 789
—, extraction of ethyl alcohol with, 327
—, from benzene 778, 780, 950
—, hydrolysis of, 782-784
—, in dyes, 782
—, oxidation of, 944
—, phenol from, 782-784
—, phenylphenol from, 785
—, reaction with acetic anhydride, 789
—, — ammonia, 786, 787
—, — benzoic acid, 805
—, — phthalide, 789
—, — potassium amide, 787, 810
—, — sodium sulphide, 785
—, triphenylamine from, 787
Chlorobenzenes, utilization of, 782
o-Chlorobenzoic acid, preparation of, 452
p-Chlorobenzylbenzoic acid, from chlorobenzene, 789
o-Chlorobenzylidene aminophenol, as antioxidant, 916
1-Chlorobutadiene, from 1,4-dichloro-2-butene, 685
—, properties of, 685
2-Chlorobutadiene, preparation of, 680
—, from chlorocyclohexene, 172
—, *see also* Chloroprene
1-Chlorobutane, *see* *n*-Butyl chloride
Chlorobutanes, dechlorination of, 806
—, from butane, 752, 1101
—, reaction with cellulose, 753
—, utilization of, 753
Chlorobutenes, from 2,2-dichlorobutane, 452
1-Chloro-2-butanol, 1-butene oxide from, 589
3-Chloro-2-butanol, ether, from 2-butene, 627
Chlorocarbonic esters, reaction with hydroxyalkylamines, 569
β-Chloro-β′-chloroisopropyl ether, preparation of, 529
Chlorocosane, definition of, 757
Chlorocresols, from chlorotoluenes, 794
2-Chlorocycloheptanol, from cycloheptene, 521
Chlorocyclohexane, from cyclohexene, 204
—, reaction with alkali, 767
—, — amines, 768
—, — cycloparaffins, 767
—, — sodium salts, 768
—, use in Grignard reaction, 767
—, utilization of, 758
Chlorocyclohexanol, preparation of, 767, 768
2-Chlorocyclohexanol, cyclohexane-1,2-diol from, 521
—, from cyclohexene, 520, 521
Chlorocyclohexene, chlorobutadiene from, 172
—, ethylene from, 172
2-Chlorocyclooctanol, preparation of, 521
Chlorocyclopentane, chlorination of, 763
—, preparation of, 763
—, pyrolysis of, 764
2-Chlorocyclopentanol, cyclopentane-1,2-diol from, 520
—, from cyclopentene, 520
Chlorodifluoromethane, from dichlorofluoromethane, 737
2-Chloro-1,2-dimethylcyclohexane, preparation of, 775
4-Chloro-1,3-dimethylcyclohexane, preparation of, 775
Chlorodimethyl ether, ethylene oxide from, 551
Chloroethanes, reaction with sulphuric acid, 829
Chloroethers, reaction with cyclohexadiene, 693, 694
—, — olefins, 613
—, — vinylacetylene, 707
β-Chloroethyl acetate, ethylene oxide from, 550
Chloroethylamines, preparation of, 570
α-Chloroethylbenzene, from styrene, 311

β-Chloroethyl-β′-chloroisopropyl ether, preparation of, 529
β-Chloroethyl chlorosulphinate, preparation of, 525
Chloroethyl methyl ketone, formation of, 611
—, lactic acid from, 451
2-Chloro-2-ethylpropane, preparation of, 513
β-Chloroethyl sulphite, preparation of, 525
Chlorofluoromethanes, from carbon tetrachloride, 736, 737
—, utilization of, 737-739
Chloroform, as dielectric, 728
—, as extraction agent, 728, 729, 1188, 1190, 1245
—, as solvent, 728
—, catalyst, in cracking, 114
—, chloropicrin from, 729
—, difluoromonochloromethane from, 737
—, estimation of, 729
—, from acetone, 430
—, from carbon tetrachloride, 807
—, from chloromethane, 727
—, in anesthetics, 728
—, in cleaning agents, 545
—, methyl chloride from, 729
—, monofluorodichloromethane from, 737
—, nitration of, 729
—, physiological effects, 1261, 1262
—, reaction with calcium fluoride and silver fluoride, 737
—, — *p*-dichlorobenzene, 729
—, — dichloroethylene, 811
—, — ethers, 345, 729
—, structure of, 728, 729
—, tri-(2,5-dichlorophenyl) methane from, 729
—, use in alcohol distillation, 327
2-Chlorohexolactone, from hex-3-enoic acid, 627
Chlorohydrin, from cycloheptene, 521
—, from glycerol, 516
Chlorohydrins, from olefinic acids, 627
—, olefin oxides from, 550
Chlorohydroquinone, as antioxidant, 916
Chloroisoamylene, reaction with hypochlorous acid, 523
Chloroisobutene, reaction with hypochlorous acid, 522
Chloroisoprene, preparation of, 721
Chloroketones, preparation of, 612, 613
Chloromethane, *see* Methyl chloride
1-Chloro-2-methoxy-2-phenylpropionic acid, from cinnamic acid, 627
Chloromethyl acetate, reaction with ethylene, 613
3-Chloro-2-methylallyl alcohol, preparation of, 797, 798
2-Chloro-2-methylbutane, *see ter*-Amyl chloride
2-Chloro-1-methylcyclohexanol, preparation of, 521
2-Chloro-1-methylcyclopentanol, preparation of, 521
α-Chloromethyl ether, reaction with olefins, 613
2-Chloro-2-methylpropane, *see ter*-Butyl chloride
1-Chloro-2-methyl-1-propene, preparation of, 509
1-Chloro-2-methyl-2-propene, preparation of, 509
Chloronaphthalenes, as solvents, 727
1-Chloro-4-naphthalenesulphonic acid, dehydration agent for di-*ter*-butylcarbinol, 401
1-Chloro-2-pentanol, 1-pentene oxide from, 589
3-Chloro-2-pentene, preparation of, 511, 513
p-Chlorophenol, from *p*-dichlorobenzene, 783, 784
—, phenol from, 784
Chlorophyll porphyrins, in petroleum, 12, 17
Chloropicrin, from chloroform, 729
—, from nitromethane, 1096
Chloroprene, co-polymerization of, 681, 682
—, formation of, 706
—, in synthetic rubber, 706
—, properties of, 681
Chloroprene, *see also* 2-Chlorobutadiene
Chloropropanes, chlorination of, 750
1-Chloro-1-propene, from propene dichloride, 508
Chloropropionic acid, lactic acid from, 451
—, preparation of, 451
2-Chloropropionyl chloride, preparation of, 609
Chlorostyrene, from methyl (chlorophenyl) chloromethane, 828
Chlorosulphonic acid, in wetting agents, 417, 1076
—, reaction with asphaltenes, 1191
—, — ceresins, 39
—, — lauryl diethylene glycol, 545
—, — naphthenic acids and aromatics, 1118
—, — olefins, 609
—, — paraffins, 32, 1102
Chloro-*n*-tetradecane, reaction with xylene, 1254
Chlorotoluene, bromination of, 795
—, from toluene, 793
—, hydrolysis of, 794
N-Chlorourea, reaction with cycloheptene, 521
—, — ethylene, 515, 516
Chromates, estimation with isopropyl alcohol, 375
Chrome alum, catalyst, ether from ethyl alcohol, 331
Chromel, catalyst, oxidation of paraffins, 874
—, —, pyrolysis of olefins, 77
Chromic acid, effect on gum formation, 924
—, catalyst, reaction of ethyl alcohol and carbon monoxide, 1041
—, —, — methyl alcohol and carbon monoxide, 1050
—, reaction with crudes, 1047
—, — isopropyl alcohol, 370
Chromic chloride, catalyst, pyrolysis of ethyl alcohol, 348
Chromic ions, catalysts, nitration of toluene, 954
Chromic oxide, catalyst, higher alcohols from ethanol, 339
—, —, oxidation of butyl alcohol, 880
—, —, pyrolysis of 2-butene, 172
—, —, — ethyl alcohol, 351, 421
—, —, — paraffins, 54, 73, 149, 1298
—, —, reduction of carbon monoxide, 1251, 1252
Chromite ore, sweetening agent, 479
Chromium, catalyst, oxidation of ethane, 872
—, —, — ethyl alcohol, 872
—, —, — methane, 869
—, —, — paraffin wax, 971
—, —, polymerization of olefins, 665
—, —, pyrolysis of alcohol, 348, 350
—, —, — hydrocarbons, 160, 185, 189
—, —, reaction of carbon disulphide and chlorine, 730
—, in cracking, 114
—, inhibitor, decomposition of ethylene oxide, 554
—, promoter, chlorination of benzene, 779
—, —, dehydrogenation of ethyl alcohol, 878
—, —, higher alcohols from ethanol, 340
—, —, oxidation of methyl alcohol, 878, 879
—, —, reduction of carbon monoxide, 1228
Chromium alloys, in cracking, 112, 134
—, in pyrolysis of hydrocarbons, 189
Chromium borate, in pyrolysis of paraffins, 160
Chromium carbonate, catalyst, oxidation of methane, 881
Chromium chloride, catalyst, decarboxylation of phthalic anhydride, 952
Chromium compounds, catalysts, hydrogenation of acetylene, 171
Chromium halides catalysts, hydration of acetylene, 712
Chromium hydroxide, catalyst, reaction of methane and steam, 278
—, —, — sulphur and hydrocarbons, 467
Chromium-lead ore, sweetening agent, 479
Chromium-nickel alloy, catalyst, polymerization of ketene, 441
—, in pyrolysis of hydrocarbons, 189
Chromium oxide, catalyst, dehydration of alcohols, 331, 420
—, —, hydration of acetylene, 714
—, —, oxidation of aromatics, 942, 945
—, —, — ethyl alcohol, 423
—, —, — hydrogen sulphide, 460
—, —, — methane, 871, 881
—, —, — *d*-*α*-pinene, 905
—, —, pyrolysis of hydrocarbons, 92, 159, 189, 227, 228
—, —, reaction of ethyl alcohol and steam, 422
—, —, — methane and steam, 278, 279
—, —, — sulphur and hydrocarbons, 467
—, —, reduction of carbon monoxide, 661, 1228
—, effect on ignition temperature, 1000

Chromium phosphate, catalyst, hydration of ethylene, *287*
Chromium salts, catalysts, acids from alcohols, 1051
—, —, reaction of olefins and carbon monoxide, 626
Chromium-silicon alloy, catalyst, acetylene pyrolysis, 89
Chromium sulphate, catalyst, ether from ethyl alcohol, 331
—, promoter, hydration of ethylene, 283
Chromous salts, catalysts, hydrogenation of acetylene, 719
Chrysene, from cracking gas, 646
—, from hydrindene, 95
—, from indene, 95
—, from natural gas, 183
—, from petroleum coke, 145
Cinnamaldehyde, cinnamyl alcohol from, 372
—, reaction with ketene, 439
—, — nitric acid, 851, 852
Cinnamates, catalysts, oxidation of paraffin wax, 971
Cinnamic acid, 1-chloro-2-methoxy-2-phenylpropionic acid from, 627
—, phenylglyceric acid from, 547, 895
—, reaction with *ter*-butyl alcohol and chlorine, 627
—, — ethyl alcohol and chlorine, 627
Cinnamyl alcohol, from cinnamaldehyde, 372
Cinnamylideneaminophenol, antioxidant, 916
Citric acid, antigelating agent, 330
—, decolorizing agent, 958
—, effect on paints, 576
—, reaction with phosphorus trisulphide, 484
Citronellal, *see* Citronell aldehyde
Citronell alcohol, blending agent for motor fuel, 1035
—, from citronell aldehyde, 372
Citronell aldehyde, citronell alcohol from, 372
Citronellol, *see* Citronell alcohol
Clark process, for cracking, 125
Clay, catalyst, alkylation of phenols, 603
—, —, chlorination of benzene, 778
—, —, hydrolysis of chlorobenzene, 782
—, —, in cracking, 112, 128
—, —, ozonization of gasoline, 1045
—, —, polymerization of olefins, 636, 666
—, —, pyrolysis of ethyl alcohol, 155
—, —, reaction of ethylene oxide and hydrogen sulphide, 564
—, decolorizing agent, 976, 977
—, desulphurizing agent, 1044
—, stabilizing agent for asphalt emulsions, 1219
—, use in refining gasoline, 134, 135, 669, 927, 928
Cleaning agents, acetic acid in, 1084
—, alcohols in, 1084
—, alkali salts in, 1112
—, carbon tetrachloride in, 731, 732, 746
—, *o*-dichlorobenzene in, 790
—, ethylene dichloride in, 745
—, ethylene glycol ethers in, 543
—, gasoline in, 746
—, glycerol in, 1112
—, hydroxyethyl ethers in, 558
—, kerosene in, 790
—, mahogany sodium sulphonate in, 746
—, methylene chloride in, 728
—, naphtha in, 746
—, naphthenic acids in, 1112
—, oleic acid in, 746
—, phosphoric acid in, 543
—, potassium sulphate in, 1112
—, red oil in, 790
—, saponin in, 543
—, sulpho detergents in, 1084
—, sulphonaphthenic acids in, 1118
—, tetrachloroethane in, 746
—, trichloropropane in, 751
Cloud point, definition of, 1176
Coagulating agent, ammonium naphthenate as, 1116
Coal, carbon from, 227
—, carbon monoxide from, 1246
—, catalyst, in cracking, 111
—, chlorination of, 227, 730
—, gasification of, 1246
—, hydrogenation of, 9
—, hydrogen from, 1246
—, lubricating oil from, 213
—, spraying with petrolatum, 41
Coal gas, as motor fuel, 27
—, ethylene from, 327, 328
—, ignition of, 1002
Coal tar, antioxidant for gasoline, 914
—, cracking of, 135
—, ethylation of, 210
Coal-tar distillates, reaction with ethylene, 593
Coal-tar oils, reaction with ethylene, 209
Coal-tar pitch, coking of, 230
Coating compositions, chlorinated paraffins in, 759
—, ethylene glycol ethers in, 543
—, formaldehyde in, 890, 891
—, from abietates, 543
—, from asphalt oil, 467
—, from casein, 1079
—, from chlorinated rubber, 543
—, from mahogany sulphonates, 1079
Cobalt, catalyst, hydration of ethylene, 291
—, —, oxidation of aromatics, 942
—, —, — ethylene, 553
—, —, — paraffin wax, 971
—, —, polymerization of pinene, 645
—, —, pyrolysis of olefins, 76
—, —, — paraffins, 158, 189
—, —, — pinene, 88
—, —, reaction of allyl bromide and hydrogen bromide, 316
—, —, — carbon and hydrogen, 1278
—, —, — methane and steam, 270, 279
—, —, reduction of carbon monoxide, 1223-1225, 1228-1230, 1232, 1233, 1236, 1237, 1240, 1242, 1244, 1249, 1250
—, effect on pyrolysis of benzene, 191
—, electrodeposition of, 571
—, promoter, chlorination of benzene, 779
—, —, in cracking, 114, 128, 129
—, —, reduction of carbon dioxide, 1242
Cobalt acetate, catalyst, oxidation of acetone, 432
—, in drying agents, 1055
—, promoter, oxidation of acetaldehyde, 885
Cobalt acetylacetonate, catalyst, phenylcyclopentane autoxidation, 907
Cobalt amines, as antiknocks, 1018
Cobalt antimonide, catalyst, dehydrogenation of alcohols, 419
Cobalt arsenide, catalyst, dehydrogenation of alcohols, 419
Cobalt bismuthate, catalyst, dehydrogenation of alcohols, 419
Cobalt boro-phosphate, catalyst, hydration of propene, 292
Cobalt bromide, detection, moisture in oil, 28
Cobalt carbonate, catalyst, methane-steam reaction, 278
—, —, oxidation of methane, 881
Cobalt chloride, reaction with ethanolamines, 570
—, — tripropanolamine, 587
Cobalt compounds, catalysts, oxidation of *d*-α-pinene, 905
—, —, sulphation of ethylene, 323
Cobalt cyanide, catalyst, sulphation of olefins, 358, 391
Cobalt fluoride, catalyst, reaction of propene and hydrogen fluoride, 307
Cobalt halides, catalysts, pyrolysis of paraffins, 158
—, —, reaction of dichloroethane and hydrogen fluoride, 747
—, —, — olefins and carbon monoxide, 625
Cobalt hydroxide, catalyst, reaction of methane and steam, 278
—, —, — sulphur and hydrocarbons, 467
Cobalt iodide, reaction with triethanolamine, 571
Cobalt naphthenate, antioxidant for lubricants, 937
—, as drying agent, 1115
—, in purification of naphthenic acids, 1105

Cobalt nitrate, catalyst, methane-steam reaction, 278
—, in cracking, 112
Cobalt nitrosocarbonyl, as antiknock, 1018
Cobalt oleate, catalysts, oxidation of *d*-α-pinene, 905
Cobalt oxide, catalyst, oxidation of aromatics, 942
—, —, — methane, 866, 881
—, —, pyrolysis of benzene, 192
—, —, pyrolysis of thiophene, 483
—, —, reaction of steam and acetylene, 714
—, —, — steam and ethanol, 422
—, —, — steam and methane, 278
—, —, — sulphur and hydrocarbons, 467
—, effect on ignition temperature, 1000
—, for removal of sulphur compounds, 397
—, promoter, in cracking, 114, 129
Cobalt phosphate, catalyst, hydration of ethylene, 284
—, —, — propene, 292
Cobalt phosphide, catalyst, dehydrogenation of alcohols, 419
Cobalt salts, catalysts, acids from alcohols, 1051
—, —, sulphation of isoolefins, 308
—, —, sulphation of propene, 358
—, reaction with triethanolamine, 572
Cobalt selenide, catalyst, dehydrogenation of alcohols, 419
Cobalt soap, catalyst, oxidation of oils, 1044
Cobalt sulphate, promoter, hydration of ethylene, 283
Cobalt sulphide, catalyst, hydration of acetylene, 712
—, —, pyrolysis of benzene, 191
Cobalt telluride, catalyst, dehydrogenation of alcohols, 419
Coconut oils, sulphates from, 1084
Coffee, decaffeination of, 710
Coke, analysis of, 145
—, as fuel, 231, 232
—, carbon from, 230-232
—, carbon black from, 222
—, carbon monoxide from, 1247
—, catalyst, in cracking, 111
—, —, pyrolysis of acetylene, 89
—, —, — paraffins, 71, 158
—, —, reaction of steam and coke-oven gas, 1247, 1248
—, —, — steam and hydrocarbons, 272, 276
—, —, reduction of carbon dioxide, 1241
—, —, reduction of carbon monoxide, 1241
—, from aromatics, 109
—, from coal tars, 135, 230
—, from crudes, 140
—, from gas oil, 102, 110
—, from lubricants, 930, 931
—, from petroleum distillates, 197
—, from petroleum residues, 229-232
—, from resins, 1189
—, hydrocarbons in, 145
—, hydrogen from, 1247
—, reaction with carbon dioxide, 1247
—, — steam, 1247
Coke-oven gas, acetylene from, 170
—, adsorption with copper oxide, 552
—, benzene from, 165
—, butene from, 165
—, carbon monoxide from, 1246-1248
—, cyclopentadiene from, 679
—, ethylene oxide from, 552
—, extraction with butanolamine, 590
—, hydrogen from, 1246-1248
—, hydrogen sulphide from, 165
—, propene from, 165
—, reaction with steam, 1247, 1248
Colloidal systems, of asphalts, 1195-1198
Color stability, effect of sulphur compounds on, 454-456
—, tests for, 925
Color stabilizers, for gasoline, 926, 927
Columbium oxide, catalyst, oxidation of aromatics, 942
Columbium pentachloride, catalyst, alkylation of aromatics, 596
Combustion, effect of carbon dioxide, 1004
—, — nitrogen, 1004
—, estimation of hydrocarbons, 1128-1132
—, — sulphur, 1127, 1162, 1163
—, flame propagation in, 1005, 1006
—, increase of pressure during, 1002-1005
—, mechanism of, 1012-1016
—, of acetylene, 1001, 1003, 1004
—, of alcohols, 999, 1004, 1005
—, of aromatics, 999, 1003-1005
—, of carbon black, 245
—, of carbon disulphide, 1003, 1004
—, of carbon monoxide, 1010
—, of fuels, mechanism, 1012, 1013
—, of hydrogen, 1003, 1004
—, of olefins, 1001, 1003-1005, 1010
—, of paraffins, 999, 1000, 1003-1005, 1011, 1012, 1014, 1015
—, of phenols, 999
—, submerged, 1061
Compression, use in ignition, 1000, 1001
Concatenation, definition of, 632
Condensation, fractional, estimation of gaseous hydrocarbons, 1132, 1133
—, aldehydes, 886, 889
Coniferous wood, resins from, 46
—, terpenes from, 46
Contact time, effect on pyrolysis of paraffins, 56, 57, 150-152, 166, 188
Co-polymerization, of 1-chlorobutadiene, 685
—, of chloroprene, 681, 682
—, of monovinylacetylene, 685
Copper, catalyst, acetone from acetaldehyde, 423
—, —, chlorination of benzene, 778, 779
—, —, cyclic ethers from dialkyl haloethers, 551
—, —, decomposition of carbon tetrachloride, 730
—, —, dehydrogenation of alcohols, 337, 340, 419, 420, 443, 878, 1051
—, —, — monoethanolamine, 568
—, —, esterification of alcohol, 339
—, —, ethers from acetals, 715
—, —, fluorination of benzene, 791
—, —, halogenation of olefins, 493
—, —, hydrogenation of acetone, 432
—, —, — acetylene, 704
—, —, — crotonaldehyde, 889
—, —, hydrolysis of chlorobenzene, 782, 783
—, —, — *o*-dichlorobenzene, 785
—, —, oxidation of alcohols, 548, 844, 879, 880
—, —, — aromatics, 942
—, —, — ethylene, 552, 553
—, —, — hydrogen, 661
—, —, — ketones, 450
—, —, — oils, 907, 932
—, —, — olefins, 893
—, —, — propene, 586
—, —, polymerization of acetylene, 704
—, —, — ketene, 441
—, —, — pinene, 645
—, —, pyrolysis of alcohol, 348, 350
—, —, — 2-butene, 172
—, —, — chlorocycloparaffins, 768
—, —, — ethylene, 172
—, —, — kerosene, 155
—, —, — methane, 158, 180, 257
—, —, — olefins, 76, 78
—, —, — paraffins, 149, 189
—, —, — pinene, 88
—, —, reaction of bromocyclohexane and amines, 772
—, —, — chlorobenzene and ammonia, 786, 787
—, —, — chlorobenzene and phenol, 788, 789
—, —, — *o*-dichlorobenzene and ammonia, 787
—, —, — ethyl alcohol and hydrogen bromide, 345
—, —, — ketones and alcohols, 443
—, —, — methyl chloride and carbon monoxide, 727
—, —, — methylene iodide and sodium sulphite, 819
—, —, — phthalic anhydride and carbon monoxide, 950
—, —, sulphation of polymerized hydrocarbons, 365
—, —, — propene, 358
—, effect on color stability, 925

Copper, effect on oxidation of transformer oil, 938, 939
—, — polymerization of butadiene, 651
—, in aging test for lubricants, 932
—, in refining gasoline, 668
—, inhibitor, decomposition of ethylene oxide, 554
—, —, oxidation of ether, 336, 337
—, promoter, hydration of ethylene, 283
—, —, in cracking, 114, 128
—, —, methane-carbon dioxide reaction, 274
—, —, oxidation of cracking gas, 881
—, —, reduction of carbon dioxide, 1242, 1247
—, —, — carbon monoxide, 1228-1232, 1236, 1237, 1240, 1241, 1249
Copper acetate, promoter, oxidation of acetaldehyde, 885
Copper acetylacetonate, catalyst, phenylcyclopentane autoxidation, 907
Copper alloys, catalysts, dehydration of alcohols, 419, 420
— in cracking, 134
Copper aluminum silicate, catalyst, reaction of phthalic anhydride and carbon monoxide, 950
Copper borate, catalyst, pyrolysis of paraffins, 160
Copper boro-phosphate, catalyst, hydration of ethylene, 285
—, —, — propene, 292
Copper bromide, catalyst, esterification of propene, 308
Copper carbonate, catalyst, decarboxylation of phthalic anhydride, 950
—, —, oxidation of petroleum, 966
—, promoter, reduction of carbon monoxide, 1231
Copper chloride, catalyst, alkylation of amines, 347
—, —, chlorination of propane, 750
—, —, esterification of propene, 308
—, desulphurizing agent, 488
—, refining agent for gasoline, 928
Copper chromate, catalyst, hydration of vinylacetylene, 705
Copper chromite, catalyst, butanol from ethanol, 341
—, —, dehydrogenation of alcohols, 420
—, —, hydrogenation of butyl lactate, 546
Copper compounds, catalyst, ethylene-sulphuric acid reaction, 323
—, effect on color stability, 938
Copper cyanide, catalyst, sulphation of isobutene, 391
Copper dish, estimation of gum formation, 910
Copper halides, catalysts, pyrolysis of paraffins, 158
—, —, reaction of dichloroethane and hydrogen fluoride, 747
—, —, — olefins and carbon monoxide, 625
Copper hydroxide, catalyst, oxidation of gasoline, 266
—, —, — petroleum, 966
Copper manganates, catalysts, hydration of vinylacetylene, 705
Copper mercaptides, formation of, 476, 477
Copper naphthenate, as antioxidant, 937
—, as preservatives, 1116
—, as wetting agent, 1117
—, catalyst, polymerization of butadiene, 651, 1116
—, in paints, 1115
—, in wood preservatives, 1115
Copper β-naphtholallylamine, as antiknock, 1018
Copper oleate, catalyst, oxidation of naphtha, 876
—, —, polymerization of butadiene, 651
Copper oxide, as sweetening agent, 667
—, catalyst, acetone from ethanol, 422, 423
—, —, alkylation of amines, 347
—, —, dioxane from β, β′-dichlorodiethyl ether, 579
—, —, dipropyl ketone from *n*-butanol, 443
—, —, esterification of alcohol, 337
—, —, ethylene oxide from ethylene chlorohydrin, 550
—, —, hydration of acetylene, 712
—, —, hydrogenation of sulphur compounds, 1248, 1249
—, —, hydrolysis of chlorobenzene, 782
—, —, methane-steam reaction, 278
—, —, oxidation of alcohols, 844, 879
—, —, — aromatics, 942
Copper oxide, catalyst, oxidation of ethane, 872
—, —, — hydrogen, 165, 190
—, —, — methane, 867, 869, 871
—, —, — olefins, 553
—, —, polymerization of ethylene, 637
—, —, pyrolysis of methane, 54
—, —, — natural gas, 227
—, desulphurizing agent, 489
—, effect on ignition temperature, 1000
—, promoter, in cracking, 112
—, —, oxidation of toluene, 950
—, —, reduction of carbon monoxide, 1231
—, refining naphthenic acids, 1109
Copper phosphate, catalyst, alcohol-carbon monoxide reaction, 339, 407
—, —, esterification of propene, 308
—, —, hydration of ethylene, 284, 291
—, —, — propene, 292
Copper protocatechualethylamine, as antiknock, 1018
Copper salicylalallylamine, as antiknock, 1018
Copper salicylalmethylamine, as antiknock, 1018
Copper salts, catalysts, acids from alcohols, 1051
—, —, ethylene oxide from ethylene chlorohydrin, 550
—, —, for sweetening, 476-478
—, —, hydration of vinylacetylene, 705
—, —, polymerization of olefins, 929
—, —, sulphation of isoolefins, 308
—, —, sulphation of propene, 358
—, extraction of olefins with, 163
—, promoters, oxidation of toluene, 950
—, —, polymerization of olefins, 634
Copper silicate, in refining gasoline, 669, 930
Copper soap, catalyst, oxidation of oils, 1044
Copper stearate, catalyst, oxidation of mineral oil, 856, 938, 939
Copper sulphate, catalyst, ether from ethyl alcohol, 331
—, —, esterification of propene, 308
—, —, ethylation of amines, 347
—, —, hydration of vinylacetylene, 705
—, —, lubricants from chlorinated paraffin, 828
—, —, oxidation of petroleum, 966
—, dehydration agent, 364
—, preparation of drying agents, 1055
—, reaction with triethanolamine, 571
Copper sulphide, catalyst, pyrolysis of benzene, 191
Copper-tin alloy, catalyst, pyrolysis of ethane, 149
Copper-uranium, catalyst, esterification of alcohol, 339
Copper vanadate, catalyst, hydration of vinylacetylene, 705
Corn, lecithin from, 728
Corn gluten, emulsifying agent, 1218
Corn oil, antioxidant for gasoline, 918
—, effect on color stability, 926
Corona discharge, action on aromatics, 260
Corrosion inhibitor, alkalies, 477
—, benzyl chloride, 794
—, copper compounds, 477
—, cyclohexene, 477
—, tetrahydronaphthalene, 477
—, zinc naphthenate, 1116, 1117
Cottonseed meal, pyrolysis of, 840
Cottonseed oil, cracking of, 136
Cracked distillates, cyclopentadiene from, 679
—, reaction with acetaldehyde, 625
—, — formaldehyde, 625
—, — α-naphthoquinone, 679
—, refining with sulphuric acid, 1075, 1076
—, sulphonic acids from, 1075, 1076
Cracked fuel, production of, 98
Cracked gasoline, butyric acid from, 854
—, characterization factor of, 1308
—, composition of, 1045
—, from Kogasin, 1252, 1253
—, glycols from, 854
—, gums from, 1054
—, oils from, 214

Cracked gasoline, reaction with ethylene, 1252, 1253
—, — furfuraldehyde, 625
—, — phenols, 604
—, resins from, 625
Cracked oils, olefins from, 161
Cracked tar, ethylene from, 155
—, voltolization of, 262
Cracking, commercial processes, 115-131
—, coke from, 109
—, effect of catalysts, 103
—, — pressure, 106, 107
—, — recycling, 109, 130
—, — temperature, 103, 104
—, effect on aromatics, 108
—, — naphthenes, 108
—, — octane number, 1033
—, — paraffins, 108
Cracking, electrical, 131
—, in distillation, 30
—, of amines, 158
—, of amylcyclohexane, 137
—, of bicyclohexyl, 137
—, of coal tars, 135
—, of crude oil, 140
—, of cyclohexane, 136
—, of decalin, 137
—, of ethylbenzene, 159
—, of gas oil, 139, 140
—, of gasoline, 136, 139
—, of kerosene, 137, 139
—, of Kogasin, 1252, 1253
—, of methane, 1017
—, of methylisopropylbicyclononane, 137
—, of naphtha, 139
—, of paraffin wax, 138
—, of propane-steam mixtures, 149
—, of sapropelite tar, 135
—, of *n*-tetradecane, free energy change, 1297
—, of wax acids, 979
—, thermodynamics of, 99-103
Cracking gas, butadiene from, 171
—, ethane from, 301
—, ethylene from, 301
—, methane from, 301
—, oxidation of, 881
—, production of, 654
—, reaction with benzene, 593, 594
—, — ethylene, 1252, 1253
—, — sulphuric acid, 359
—, removal of olefins from, 324
—, utilization of, 164, 631, 654
Cracking oil, detergents from, 1083
Cracking residuum, effect on pyrolysis of paraffins, 158
Creosote, extraction with isopropyl alcohol, 373
Creosote, lampblack from, 242
—, reduction of, 264
Cresol, antioxidant for gasoline, 914, 915
—, extraction agent for alcohols, 360, 391
—, from chlorotoluene, 794
—, in lubricating oils, 43
—, reaction with acetylene, 715
o-Cresol, from ethyl alcohol, 173
—, reaction with *ter*-butyl alcohol, 416
m-Cresol, antioxidant for transformer oil, 941
—, reaction with ammonia, 788
—, — *ter*-butyl alcohol, 412
—, *m*-toluidine from, 788
m-Cresol methyl ether, reaction with *ter*-butyl alcohol, 416
p-Cresol, stabilizing agent for methyl chloride, 727
Cresylic acid, extraction agent for olefins, 163
Critical compression ratio, definition of, 1024
—, relation to boiling point, 141
Critical oxidation potential, definition of, 920
Critical pressure, determination of, 1313-1318
Critical solution temperature, determination of, 1178, 1180
Critical temperature, determination of, 1311-1313
—, critical pressure from, 1314, 1315, 1318
Cross process, for cracking, 118
Crotonaldehyde, butanol from, 889
—, butyraldehyde from, 889
—, crotyl alcohol from, 372
Crotonaldehyde, extraction of lubricating oils with, 43
—, from acetaldehyde, 878, 889
—, hydrogenation of, 889
Crotonic acid, dihydroxybutyric acid from, 547
Crotyl alcohol, from crotonaldehyde, 372
Crotyl bromide, reaction with hypochlorous acid, 523
Crude oil, acids in, 10, 21
—, adamantane in, 35
—, albuminous substances in, 12
—, aquolysis of, 132
—, aromatics in, 13, 31, 32, 35, 1149
—, asphaltenes in, 13, 1189, 1190
—, asphaltogenic acids in, 1194, 1195
—, carbon dioxide in, 10
—, ceresin in, 13
—, characterization factors of, 1308
—, composition of, 10-12, 29, 46
—, cracking of, 97, 140
—, emulsifying agents from, 1217
—, emulsions in, 10
—, enthalpy-temperature relations, 1334, 1335
—, entropy-temperature relations, 1340, 1341
—, fractionation of, 21, 24, 28, 31, 34, 97, 116
—, inorganic constituents of, 46-48
—, naphthalene from, 179
—, naphthenes in, 10, 13, 31-34, 1149
—, naphthenic acids in, 10, 1103, 1104
—, nitrogen compounds in, 10, 17
—, nitrotoluene from, 35
—, optically active constituents in, 12, 17
—, origin of, 16-21
—, oxidation of, 938, 1190
—, oxygenated compounds in, 17
—, paraffins in 10, 13, 32, 33, 1149
—, phenols in, 10
—, porphyrins in, 12, 17
—, refining of, 28
—, resins from, 1189
—, specific heat determination, 1323
—, sulphur compounds in, 10-12, 17
—, water in, 10
—, vanadium in, 20, 46, 47
—, world consumption, 10
—, world production, 7
Crystal oil, viscosity of, 15
Cumarone, in gasoline, 144
Cumene, from benzene, 382, 383, 402
—, from pinene, 88
Cuprene, preparation of, 704
—, utilization of, 704
Cupric acetate, catalyst, esterification of alcohol, 338
Cupric chloride, catalyst, chlorination of benzene, 778
—, —, — ethane, 741
—, —, — methane, 726
—, —, — perchloroethylene, 742
—, —, —propane, 750
—, —, ethylene chlorohydrin from ethylene, 515, 516
—, —, pyrolysis of ethyl alcohol, 348, 351
—, —, reaction of acetylene and aniline, 719
—, —, reaction of 2-butene and chlorourea, 509
—, in preparation of fumigants, 566
—, reaction with mercaptans, 477
—, refining agent for oils, 1044
Cupric compounds, catalysts, oxidation of hydrocarbons, 1043
Cupric oxide, catalyst, oxidation of ethane, 1131
—, —, — hydrocarbons, 1049
—, —, — methane, 1128
—, —, — paraffin oils, 907, 931
—, —, reaction of alcohols and ketones, 443
—, —, — methyl chloride and formaldehyde, 727
Cupric phosphate, catalyst, hydrolysis of chlorobenzene, 783
Cuprous chloride, absorption of acetylene by, 1124
—, — carbon monoxide by, 1124, 1125
—, — diolefins by, 165, 175, 359, 391
—, catalyst, chlorination of vinylacetylene, 687
—, —, hydrolysis of chlorobenzene, 782, 783
—, —, polymerization of acetylene, 704, 705
—, —, reaction of acetylene and aniline

Cuprous chloride, catalyst, reaction of carbon monoxide and benzene, 957
—, —, — ethylene and sulphuric acid, 322, 323
—, —, — ethylene dichloride and ammonia, 497
—, —, — hydrogen chloride and acetylene, 716
—, —, — hydrogen chloride and isopropenylacetylene, 721
—, —, — hydrogen chloride and vinylacetylene, 680, 706
—, reaction with ethylene, 163
Cuprous cresolate, absorption of ethylene by, 164
Cuprous cyanide, catalyst, sulphation of ethylene, 323
—, —, — propene, 358
Cuprous formate, absorption of carbon monoxide by, 234
Cuprous lactate, absorption of carbon monoxide by, 234
Cuprous nitrate, absorption of ethylene by, 164
Cuprous oxide, catalyst, hydration of propene, 360
—, —, hydrolysis of chlorotoluene, 794
—, —, reaction of chlorobenzene and ammonia, 786
—, —, — ketones and alcohols, 443
—, —, — propene and phosphoric acid, 358
—, —, sulphation of ethylene, 323
—, inhibitor, decomposition of ethylene oxide, 554
—, —, peroxides in ether, 335
—, reaction with *p*-dichlorobenzene, 784
Cuprous phenolate, absorption of ethylene by, 164
Cuprous salicylate, absorption of ethylene by, 164
Cuprous salts, catalyst, polymerization of acetylene, 704
Cyanamide, as antiknock, 1018
Cyanic acid, as antiknock, 1018
Cyanides, reaction with alkyl halides, 822
Cyanoanilide, as antiknock, 1018
Cyanobutadiene, from cyclohexenenitrile, 172
Cyanogen, ignition temperature of, 987
Cyanohydrins, from aldehydes, 886
—, hydrolysis of, 886
Cyclic acetals, from polyhydric alcohols and acetylene, 715
—, — and aldehydes, 544
Cyclic alcohols, esterification of, 1118-1120
Cyclic sulphones, from diolefins, 176
Cyclobutane, halogenation of, 762, 763
1,3-Cyclobutanedione, from ketene, 441
Cyclobutanol reaction with hydrogen bromide, 762
Cyclobutanone, preparation of, 762
Cyclobutene, reaction with halogens, 762
Cyclobutylmethanol, reaction with hydrogen bromide, 764
Cycloheptane, dehydrogenation of, 94
Cycloheptene, reaction with N-chlorourea, 521
Cyclohexadiene, auto-ignition of, 1017
—, effect of lead tetraethyl on, 1022
—, from *n*-butene, 81
—, reaction with aryl halides, 693, 694
—, — bromoacetamide, 531
—, — chloroethers, 693, 694
—, — methyl hypobromite, 531
—, — triphenylchloromethane, 694
1,3-Cyclohexadiene, *see* Cyclohexadiene
Cyclohexadiene oxide, from cyclohexadiene dibromide, 589
—, reaction with perbenzoic acid, 589
—, — phosphorus pentabromide, 589
Cyclohexane, action of aluminum chloride on, 204, 206, 445
—, as anesthetic, 1266, 1267
—, bicyclohexyl from, 205
—, bromination of, 769, 770
—, catalyst, reaction of propene and hydrogen bromide, 306
—, chlorination of, 765-767
—, condensation of, 205
—, cracking of, 101, 111, 136
—, dehydrogenation of, 92, 101, 185, 204, 1041
—, effect of lead tetraethyl on, 1022
—, effect on peroxide formation, 923
—, — ethylation of, 205
—, — photochemical decomposition of acetone, 450
—, explosive characteristics of, 1011, 1017
—, extraction agent for polymerized hydrocarbons, 397
Cyclohexane, fluorination of, 773, 774
—, free energy of formation, 1225, 1226
—, —, effect of temperature on, 1295
—, from benzene, 1298
—, from *n*-butene, 81
—, from di-*n*-heptyl mercury, 71
—, from *n*-hexane, 198
—, from methylcyclohexane, 206
—, from methylcyclopentane, 89
—, from *n*-tetradecane, 1297
—, in crude oil, 33, 34
—, inflammability limits of, 980-982
—, in gasoline, 13, 144
—, 1-methyl-2-acetylcyclopentane from, 205
—, methylcyclopentane from, 205, 206, 1101
—, —, free energy change, 1301, 1302
—, molal entropy, 1290
—, oxidation of, 854, 855, 874, 876
—, peroxide from, 854, 855
—, photochemical decomposition of, 267
—, pyrolysis of, 92, 93, 136, 172, 185, 205, 208
—, reaction with acetylchloride, 204, 445, 1101
—, — ethylene, 601, 602
—, — halides, 1102
—, — monochlorocyclohexane, 767
—, — nitrogen tetroxide, 1091
—, — steam, 273
—, stability of, 1286
—, use in alcohol distillation, 327
Cyclohexane carboxylic acid, preparation of, 767
Cyclohexanediol, from cyclohexene, 895
—, reaction with hydrogen bromide, 770
1,2-Cyclohexanediol, from 2-chlorocyclohexanol, 521
1,4-Cyclohexanediol, reaction with thionyl chloride, 766
Cyclohexane homologues, boiling points, 16
—, effect on knock rating, 1024, 1025
—, in crude oil, 33
—, pyrolysis of, 89
Cyclohexanol, as extraction agent, 42
—, octane number of, 1028
—, oxidation of, 444
—, reaction with acetic acid, 405
—, — amines, 614
—, — bromine, 770
—, — formic acid, 406
—, — hydrogen bromide, 769, 770
—, — naphthalenesulphonic acid, 410
—, — phosphorus tribromide, 770
—, — thionyl chloride, 766
Cyclohexanone, adipic acid from, 895
—, as dewaxing agent, 453
—, as extraction agent for acetylene, 469
—, catalyst, decomposition of ketones, 450
—, from nitrocyclohexane, 1095
—, in blended fuels, 915
—, oxidation of, 450, 451
Cyclohexene, action of aluminum chloride on, 204
—, auto-ignition of, 1017
—, autoxidation of, 907
—, bromination of, 770
—, butadiene from, 93
—, chlorination of, 767
—, corrosion inhibitor, 477
—, cyclohexanediol from, 895
—, cyclohexenylcarbinol from, 624
—, dehydrogenation of, 185-187
—, effect of lead tetraethyl on, 1022
—, entropy of formation, 1284, 1285
—, free energy of formation, 1284, 1285
—, from bromocyclohexane, 773
—, from cyclohexane, 204
—, halohydrin from, 520, 521, 626
—, heat of formation, 1284, 1285
—, 2-hydroxycyclohexylcarbinol from, 624
—, inflammability limits of, 980, 981, 982
—, iodoalkyl nitrate from, 629
—, molal entropy, 1284, 1285
—, monochlorocyclohexane from, 204
—, monochloropolycyclohexyl from, 204
—, octane number of, 1028
—, oxidation of, 852, 895, 898, 901
—, polymerization of, 204, 645

Cyclohexene, reaction with acetyl chloride, 612
—, — acetyl iodide, 611
—, — benzene, 592, 595
—, — butadiene, 186
—, — *ter*-butyl hypochlorite, 518
—, — *a*-chloromethyl ether, 613
—, — dichloroacetic acid, 313
—, — hypobromous acid, 531
—, — iodine, 774, 775
—, — mercuric acetate, 628
—, — mercuric nitrate and iodine, 629
—, — phenol, 605
—, — phenylacetyl chloride, 613
—, — steam, 273
—, — sulphur dioxide, 616, 617
—, — sulphuric acid, 392
—, — trichloroacetic acid, 313
Cyclohexene carboxylic acid, reaction with acetyl chloride, 612
Cyclohexene chlorohydrin, from cyclohexene, 626
Cyclohexenenitrile, cyanobutadiene from, 172
Cyclohexene number, definition of, 919
Cyclohexene oxide, preparation of, 589
—, reaction with magnesium dimethyl, 589
—, — mercaptans, 472
Cyclohexene peroxide, properties of, 898
1-Cyclohexen-3-ol, preparation of, 898
Cyclohexenylcarbinol, from cyclohexene, 624
Cyclohexylallene, pyrolysis of, 94
Cyclohexylaminophenols, antioxidants, 916
Cyclohexylaniline, preparation of, 768, 772
Cyclohexyldimethylcarbinol, preparation of, 450
Cyclohexylformaldehyde, preparation of, 521
Cyclohexyl methyl ketone, preparation of, 205
Cyclohexylphenol, preparation of, 605
3-Cyclohexylpropene, reaction with sulphur dioxide, 618
μ-Cyclohexyltridecanoic acid, preparation of, 771
Cycloolefins, estimation of, 1152
—, reaction with selenium dioxide, 895
—, — sulphur, 455, 456
Cyclooctane, *p*-xylene from, 94
Cycloparaffins, aromatics from, 185, 186
—, cracking of, 111
—, dehydrogenation of, 33, 186
—, effect on knock rating, 1024, 1025
—, from paraffins, 18, 71
—, in crude oil, 32, 33
—, molal entropy, 1290
—, octane numbers of, 1028
—, pyrolysis of, 89-95, 148, 185, 186
—, reaction with sulphuric acid, 1082
—, stability of, 101
—, *see also* Naphthenes
Cycolopentadiene, bromination of, 684, 700
—, chlorination of, 763
—, effect of lead tetraethyl on, 1022
—, from alcohols, 676
—, from coke-oven gas, 679
—, from cracked distillates, 679
—, from cracking gas, 645, 646
—, from cyclopentane, 90
—, from kerosene, 144, 171
—, from propane, 60, 182
—, in gasoline, 144
—, polymerization of, 652, 654
—, reaction with 2-bromoazobenzene, 693
—, — diazonium chlorides, 700
—, — hydroxyazo compounds, 692, 693
—, — maleic acid, 945
—, — quinoneazine, 693
Cyclopentadiene derivatives, effect of lead tetraethyl on, 1020
—, from alkylated diethyl malonates, 676
—, uses of, 676
Cyclopentadiene polymers, structure of, 652
Cyclopentane, action of radon on, 267
—, effect of lead tetraethyl on, 1022
—, effect on knock rating, 1024, 1025
—, from cyclohexanes, 206
—, halogenation of, 763-765
—, in crude oil, 10, 33
—, in gasoline, 13, 33
—, oxidation of, 876, 1043
Cyclopentane, pyrolysis of, 90
—, stability of, 1286
Cyclopentane homologues, boiling points, 16
—, stability of, 91
Cyclopentanol, reaction with hydrochloric acid, 763
—, — phosphorus tribromide, 764
1,2-Cyclopentanediol, from 2-chlorocyclopentanol, 520
Cyclopentene, action of radon on, 267
—, chlorohydrin from, 520
—, effect of lead tetraethyl on, 1022
—, effect on knock rating, 1024, 1025
—, from chlorocyclopentane, 764
—, from cyclopentane, 90
—, reaction with acetyl chloride, 612, 613
—, — bromine, 764
Cyclopentyl carbinol, preparation of, 763, 764
Cyclopentylformaldehyde, from 2-chlorocyclohexanol, 521
Cyclopropane, as anesthetic, 750, 1256, 1265-1269
—, explosive property of, 1268
—, hydrogenation of, 761
—, isomerization of, 90
—, photochemical decomposition of, 265
—, reaction with benzene, 596
—, — bromine, 761
—, — chlorine, 760, 761
—, — isobutane, 602
Cyclopropene, from dibromocyclopropane, 762
—, isomerization of, 88
—, reaction with bromine, 761, 762
Cylinder oil, cracking of, 137
—, in detergents, 1073
—, oxidation of, 1043
Cymene, from pinene, 88
—, from toluene, 382, 401, 402
—, reaction with *ter*-butyl alcohol, 412, 416

D

De-alkylation, of aromatics, 37
Decaethylene glycol, preparation of, 544, 545
Decahydronaphthalene, decomposition of, 206
—, diluent, acetylene polymerization, 703
—, in motor fuel, 1039
Decalin, autoxidation of, 907
—, cracking of, 93, 137
—, reaction with aluminum chloride, 206
Decane, chlorinated, reaction with benzene, 758
—, from carbon monoxide and hydrogen, 1245
—, from petroleum, 32
Decarbonizing, by carbon tetrachloride, 731
—, by chlorobenzene, 782
—, by *o*-dichlorobenzene, 790
—, by oleic acid, 790
—, by triethanolamine, 790
Decene, in gasoline, 144
—, from chlorinated paraffins, 807
Dechlorination, of acetylene tetrachloride, 710
Decolorizing agents, for asphalts, 1192
—, preparation of, 486
Decolorizing, by clay, 976, 977
3-Decyn-1-ol, preparation of, 565
DeFlorez process, of cracking, 120
Dehalogenation, of chlorinated kerosene, 807
Dehydration, of ethyl alcohol, 328, 329, 330, 1051
—, of glycols, 548
—, of hydroxy-acids, 968
—, of isopropyl alcohol, 173
—, of tertiary alcohols, 394, 901
Dehydroacetic acid, from acetylketene, 442
Dehydrogenation, of acenaphthene, 955
—, of alcohols, 173, 337, 348, 878, 1051
—, of cyclohexene, 185, 186
—, of ethylbenzene, 156
—, of naphthenes, 31, 33, 89, 91, 92, 94, 141, 1041, 1149, 1150
—, of paraffins, 94, 99, 101, 107, 148, 149, 158
—, —, free energy change, 1284, 1298
—, of thiophane, 484
—, of 1,1,4-trimethylcycloheptene, 94
De-inking agents, sulphates as, 1086
Demethanation, of dicyclopentadiene, 156
Demethylation, in pyrolysis, 101

Demulsibility, of asphalt emulsions, 1221
Demulsifying agent, ammonium naphthenate as, 1116
—, black kontakt as, 1075
—, calcium chloride as, 1105
—, ethyl alcohol in, 1075
—, fatty acids in, 1075
—, gas oil as, 1107
—, kerosene in, 1075
—, lubricating oil in, 1115
—, naphthenic acids as, 1111, 1112, 1114
—, oxidized castor oil in, 1075
—, sodium chloride as, 1108, 1111, 1112
—, sodium hydroxide as, 1111, 1112
—, sulphates as, 1085, 1086
—, sulphonic acids as, 1074, 1075, 1116
Denaturants, from acid sludge, 486
—, by oxidation of distillates, 1053
Denigès' reagent, detection of isopropyl alcohol, 371
Denoxol, denaturant, 876
Denoxol-Solve, gum inhibitor, 876
Density determinations, in gas analysis, 1134, 1135
Depolymerization, of olefins, 101
Derris, in insecticides, 1078
Desoxo-phyllerythrin, in oil shale, 19
Desoxophyllerythroatioporphyrin, in oil shale, 19
Destructive distillation, theory of, 16
Desulphurization, of gases, 1044
Desulphurization, with ozone, 1044, 1045
Desulphurizing, with hydrogen, 670
Detektol O. Special, odorizer, 876
Detergents, ammonium sulphonate as, 1069
—, cylinder oil in, 1073
—, from cracking oil, 1083
—, from ethylene chlorohydrin, 526
—, from fatty acids, 1084
—, from mercaptans, 487
—, Igepons as, 1082
—, naphthenic acids in, 1112
—, oleyl ethylene diamine as, 809
—, spindle oil in, 1073
—, sulphate, sulphonates in, 1086
—, sulphates in, 1073, 1074, 1082-1086
—, sulphonaphthenic acids in, 1112
—, sulphonic acids in, 1069, 1073, 1074, 1082-1086
—, urea in, 1073
—, wax acids in, 978
Deurag, composition of, 26
Deuterioacetaldehyde, formation of, 725
Deuterioacetylene, polymerization of, 266, 725
—, synthesis of, 724, 725
Deuteriobenzene, preparation of, 273
Deuteriochloroform, preparation of, 729
Deuterium, in benzene, 206
—, inflammability limits of, 982, 983
Deuterium chloride, action on benzene, 207
Deuterium oxide, reaction with benzene, 260, 273
—, — calcium carbide, 743
—, — trichloroacetaldehyde, 729
Dewaxing, of lubricants, 744, 745, 1044
—, of residual oils by propane, 46
—, with butyl alcohol, 728
—, with carbon tetrachloride, 731
—, with chlorobenzenes, 782
—, with chlorofluoromethanes, 738, 739
—, with ethyl chloride, 738, 739
—, with methyl chloride, 738, 739
—, with methylene chloride, 728
—, with naphtha, 728
Diacetone alcohol, from acetone, 427, 430
—, from mesityl oxide, 430
—, motor fuel from, 1040
—, use as solvent, 427
Diacetylene, acetone solvent for, 170
—, butadiene from, 677, 678
—, from petroleum hydrocarbons, 255
2, 3-Dialkyldioxanes, preparation of, 581
Dialkyl oxalates, as antiknocks, 1017
Dialkyl phthalates, as antiknocks, 1017
Dialkyl sulphates, hydrolysis of, 325, 326, 327
—, preparation of, 392
Diallyl, pyrolysis of, 88
o-Diaminobenzene, from *o*-dichlorobenzene, 787
Diaminodiphenylamine, as antioxidant, 917
Diaminofluorenes, as antioxidants, 918
1,2-Diamino-2-methylpropane, *see* Isobutenediamine
Diaminophenols, as antioxidants, 916
Diamylamine, reaction with 1,10-dichlorodecane, 810
Diamyl ether, from ethyl alcohol, 337
sec-Diamyl sulphate, preparation of, 309
Diaryl arylenediamines, as antioxidants, 917
Diaryl ethers, from chlorobenzenes, 782
Diarylguanidines, as antioxidants, 915
Diaryl hydrocarbons, refining of, 193
Diaryl ketones, from chlorobenzenes, 782
Diaryl dioxanes, preparation of, 581
Diazines, from cottonseed meal, 840
Diazoaminobenzene, catalyst, polymerization of butadiene, 651, 673
Diazomethane, reaction with trichloroacetyl glycol, 540
Diazonium chlorides, reaction with olefins, 700
2,3,10,11-Dibenzoperylene, from phenanthrene, 208
Dibenzylperylenes, as antioxidants, 918
Dibenzoyl peroxide, catalyst, esterification of olefins, 318
Dibenzylamine, reaction with olefin oxides, 560, 589
β-Dibenzylaminoethyl alcohol, preparation of, 560
1-Dibenzylamino-2-methyl-2-propanol, preparation of, 589
Dibenzyl-amino-phenol, as antioxidant, 916
Dibiphenylene ethylene, reaction with amines, 615
—, — ammonia, 615
Dibromoallyls, preparation of, 315, 316
Dibromoamine, reaction with ketene, 440
Dibromobenzene, from benzene, 791
1,2-Dibromobutane, reaction with sodium amide, 829
1,4-Dibromobutane, from butadiene, 684, 685
1,4-Dibromobutene, preparation of, 683
Dibromocyclobutane, hydrolysis of, 762, 763
—, preparation of, 762
—, reaction with bromine, 763
Dibromocyclohexane, preparation of, 770
—, reaction with phthalimide, 772
—, — quinoline, 772
Dibromocyclopentane, preparation of, 764
Dibromocyclopropane, cyclopropene from, 762
—, hydrolysis of, 762
β,β′-Dibromodiethyl ether, reaction with aniline, 583
Dibromomethylcyclohexanes, preparation of, 775
1,2-Dibromopentane, dehalogenation of, 514
1,4-Dibromopentane, preparation of, 763
Dibromopropanes, preparation of, 315
Dibutadiene, antiknock properties of, 1027, 1028
Dibutanolamine, preparation of, 588
Di-β-butoxyethyl ethyleneglycol diphthalate, preparation of, 542
Di-*ter*-butylcarbinol, *see* 2,2,4,4-Tetramethylpentanol-3
Dibutylamine, catalyst, ethylene dichloride-sodium polysulphide reaction, 499
—, —, vinylacetylene-hydrogen sulphide reaction, 709
Dibutylbenzenes, preparation of, 208, 592, 594
2,3-Di-*ter*-butyl-1,3-butadiene, preparation of, 679
Dibutyl ether, preparation of, 337
—, pyrolysis of, 87
Di-*ter*-butylethylene, formation of, 411
Di-*n*-butyl ketone, from *n*-valeric acid, 446
Dibutylnaphthalenesulphonamide, reaction with ethylene oxide, 562
Dibutylnitrosoamine, use in fuels, 1098
2,4-Dibutyl-*ter*-butylphenol, preparation of, 418
Dibutyl phthalate, stabilizer for gasoline, 915
Dibutyl phthalate, use, as absorbent, 738
Dibutyl sulphate, from butenes, 309, 392
Di-*ter*-butyl sulphate, reaction with hydrogen sulphide, 463
Dibutyl sulphone, extraction agent, 486
Dicarboxylic acid chlorides, preparation of, 945
Dicarboxylic acids, from diolefins, 698

Dichloroacetic acid, from pentachloroethane, 830
—, reaction with cyclohexene, 313
—, — isopropyl alcohol, 376
—, — propene, 308
asym-Dichloroacetone, from acetone-chlorine reaction, 430
ω,ω-Dichloroacetophenone, from phenylacetylene, 626
Dichloro-*ter*-amyl alcohol, preparation of, 523
o-Dichlorobenzene, as cleansing agent, 790
—, as paint remover, 790
—, as solvent, 543, 546, 790
—, *o*-diaminobenzene from, 787
—, dewaxing agent, 433, 495, 507
—, fluorination of, 792
—, hydrolysis of, 785
—, in analysis of graphite grease, 789
—, in decarbonizing, 790
—, in lubricants, 790
—, reaction with ammonium hydroxide, 787
—, — sulphonyl chloride, 782
p-Dichlorobenzene, *p*-chlorophenol from, 783, 784
—, from benzene, 781
—, in motor fuel, 1039
—, reaction with chloroform, 729
—, — cuprous oxide, 784
—, tri-(2,5-dichlorophenyl) methane from, 729
Dichlorobenzenes, chlorination of, 781
—, in insecticides, 790
1,2-Dichlorobutadiene, polymerization of, 687
2,3-Dichlorobutadiene, from 1,2,3,4-tetrachlorobutane, 686, 687
2,2-Dichlorobutane, preparation of, 452
2,3-Dichlorobutane, solvent for fats, 753
Dichlorobutanes, from butane, 752
—, pyrolysis of, 678
1,2-Dichlorobutene, from butadiene, 685
—, from monovinylacetylene, 687
—, polymerization of, 685
1,4-Dichlorobutene, from butadiene, 685
—, polymerization of, 685
1,4-Dichloro-2-butene, dechlorination of, 685
3,4-Dichloro-1-butene, reaction with potassium hydroxide, 680, 681
Dichlorobutenes, monovinylacetylene from, 685
Dichloro-*ter*-butyl alcohol, epichlorohydrin from, 523
—, from chloroisobutene, 521
—, β-methyl glycerol from, 523
1,2-Dichlorocyclohexane, preparation of, 767
—, pyrolysis of, 767, 768
Dichlorocyclopropane, formation of, 761
1,10-Dichlorodecane, reaction with diamylamine, 810
Dichlorodiacetylene, from hexachlorobutane, 510
Dichlorodialkylether, from olefins, 628
β,β′-Dichlorodiethyl ether, N-alkyl morpholines from, 583
—, as extraction agent, 30, 31, 515, 529, 530
—, as solvent, 30, 43, 727
—, dioxane from, 579
—, di-β-phenylethyl ether from, 529
—, divinyl ether from, 528
—, ethylene oxide from, 551
—, for absorption of olefins, 163
—, in dewaxing, 530
—, preparation of, 528
—, reaction with alkalies, 528
—, — ammonia, 583
—, — aniline, 528, 583
—, — phenols, 528
—, — phenylhydrazine, 583
—, — sodium polysulphide, 528
Dichlorodiethyl sulphide, detection of, 619
—, from ethylene, 619
Dichlorodifluoromethane, as refrigerant, 737, 738
—, from carbon disulphide, 737
—, from carbon tetrachloride, 733, 734
—, from difluoromethane, 734, 735
—, from monofluorotrichloromethane, 737
—, diluent, fluorination of benzene, 792
—, in fractional crystallization, 31
—, in charging cream, 739
β,β′-Dichlorodiisopropyl ether, preparation of, 530
2,3-Dichlorodioxane, preparation of, 581
2,3-Dichloro-1,4-dioxane, reaction with trimethylene glycol, 549
Dichloroethane, determination of, 744
—, extractant for sulphur, 745
—, hydrolysis of, 797
—, reaction with ammonia, 808, 809
—, — *sym*-dichloroethylene, 811
—, — hydrogen fluoride, 747
—, — oleic acid, 815
—, — trichloroethylene, 811
—, — vinyl chloride, 811
—, solvent for naphthalene, 745
—, use in cracking, 114
—, uses for, 745
Dichloroethylene, as extraction agent, 1245
—, preparation of, 711
Dichlorofluoromethane, monochlorodifluoromethane from, 737
1,4-Dichlorohexane, preparation of, 766
1,3-Dichloroisobutane, in de-inking paper, 753
Dichloromethane, entropy chart, 1337
—, from carbon tetrachloride, 807
—, *see* Methylene chloride
1,3-Dichloro-2-methylbutane, formation of, 513
2,3-Dichloro-2-methylbutane, formation of, 513
1,2-Dichloro-2-methylpropane, hydrolysis of, 797
1,3-Dichloro-2-methylpropane, use in dewaxing oils, 753
Dichloropentamethylenetetramine, reaction with benzene, 779
Dichloropentane, in varnish remover, 755
—, *see also* 1-Amylene dichloride
Dichlorophenyl methane, reaction with ethers, 345
Dichloropropane, from cyclopropane, 761
1,2-Dichloropropane, as fumigant, 751
—, *see also* Propene dichloride
Dicyanodiamide, as antiknock, 1018
Dicyanoperylenes, as antioxidants, 918
Dicyclohexene, antiknock properties of, 1027, 1028
1,1′-Dicyclohexene, reaction with ozone, 902
Dicyclohexyl oxalate, from cyclohexanol, 406
Dicyclopentadiene, bromination of, 700
—, decomposition of, 652
—, demethanation of, 156
Dielectric constant, definition of, 789
Dielectrics, ceresin in, 1255
—, from chlorobenzenes, 782
—, from chloroform, 728
—, from ethylene dichloride, 789
—, from pentachlorobiphenyl, 789
—, from trichlorobenzene, 789
Die lubricants, preparation of, 731
Diesel fuel, cetene as reference standard, 1033, 1034
—, from carbon monoxide and hydrogen, 1250
—, from cracked distillates, 126
—, Kogasin as, 1253
—, mesitylene as reference standard, 1033
Diethanolamine, for absorption of olefins, 164
—, gum inhibitor, 915
—, in washing textiles, 575
—, morpholine from, 583
—, preparation of, 567
—, reaction with calcium bromide, 572
—, — trinitrotoluene, 570
Diethers, from ethylene glycol, 889
Diethinylcyclobutane, preparation of, 705
Diethylamine, *ter*-amines from, 809
—, catalyst, condensation of aldehydes, 889
—, in preparation of hydroxyalkylcellulose, 559
—, reaction with ethylene chlorohydrin, 527
Diethylaminoethanol, preparation of, 568
Diethylaniline, preparation of, 346
Diethylbenzene, from ethylbenzene, 208
o-Diethylbenzene, in gasoline, 144
Diethyl carbonate, solvent for acetylene, 169
1,2-Diethylcyclohexene, naphthalene from, 94
Diethylene glycol, dehydration agent, 538
—, fatty acid esters, toxicity of, 549
—, from ethylene glycol, 544, 577
—, in heat transfer media, 539
—, in pressure transfer media, 539
—, in tobacco, 546

Diethylene glycol, in wetting agents, 1076
—, reaction with ethylene oxide, 558
—, — nitric and sulphuric acids, 546
—, sodium salt, reaction with hexaethylene glycol, 544, 545
Diethylene glycol butyl ether, as solvent, 546
—, in brake fluid mixtures, 546
Diethylene glycol dinitrate, preparation of, 546
Diethylene glycol ethers, as solvents, 543
Diethylene glycol ethyl ethers, in brake fluid mixtures, 546
Diethylene glycol formal, as solvent, 542, 543
Diethylene glycol isobutyrate, plasticizer for cellulose acetate, 540
Diethylene glycol monoethyl ether, in condensers, 545
Diethylene glycol monoethyl ether, reaction with boric acid, 545
Diethylene glycol propionate, in cellulose compositions, 546
Diethyl ether, as blending agent, 1035, 1038
—, as extraction agent, 300, 1070, 1245
—, catalyst, oxidation of hydrocarbons, 862
—, decomposition of, 334, 335
—, dehydration of, 538, 578
—, estimation of paraffin wax, 1155
—, ethyl alcohol from, 332, 333, 334
—, ethylene from, 334
—, from ethyl alcohol, 330, 331, 332
—, from ethyl chloride, 797
—, from ethylene oxide, 558
—, ignition temperature of, 987, 988, 989
—, in motor fuels, 1039
—, inflammability limits of, 980, 985
—, oxidation of, 335
—, peroxides from, 335, 336, 337
—, reaction with hydrogen chloride, 345
—, solvent for ketene, 435
Diethyl ether-gasoline blends, as motor fuels, 1038
α-Diethyl-ethylene chlorohydrin, preparation of, 520
Diethyl fumarate, reaction with monoethanolamine, 569
Diethyl ketone, as solvent, 681
—, from propionic acid, 446
—, reaction with calcium hypochlorite, 453
—, triethyl carbinol from, 457
Diethyl magnesium, reaction with olefin oxides, 586, 588
Diethyl maleate, antioxidant, 915
Diethyl malonates, alkylated, cyclopentadiene derivatives from, 676
Diethyl oxalate, solvent for acetylene, 169
3,3-Diethylpentane, in shale oil, 33
Diethyl pentasulphide, preparation of, 481, 482
Diethylpinacone, reaction with alum, 678
Diethyl phthalate, decarboxylation of, 952
Diethyl sulphate, ethyl acetate from, 305
—, ethyl alcohol from, 326, 327
—, ethylating agent, 300
—, ethyl ether from, 326
—, formation of, 298-300, 321
—, hydrolysis of, 300
—, reaction with calcium acetylide, 722
—, — hydrogen chloride, 327
—, — monoethanolamine, 568
Diethyl sulphide, from ethylene oxide-potassium thiocyanate reaction, 564
Diethyl thiosulphite, preparation of, 345, 346
Diethyl *o*-tolyl ammonium chloride, 808
Diethyl trisulphide, action on metals, 481
—, oxidation of, 481
—, preparation of, 481
Difluoromethane, from methylene chloride, 734
—, reaction with chlorine, 734, 735
Difluoromonochloromethane, from chloroform, 737
Difuroyl peroxide, reaction with sodium methoxide, 1152
Diglycolic acid, from dioxane, 580
Dihalides, reaction with mercaptans, 485
Dihaloethanes, hydrolysis of, 532
Dihaloperylenes, as antioxidants, 918
Di-*n*-heptyl ketone, from caprylic acid, 446
Di-*n*-heptyl mercury, pyrolysis of, 71
Dihydrobiphenyl, from benzene, 259
Dihydrobenzene, from cyclohexane, 93
Dihydrochaulmoogric acid, use in leprosy treatment, 771, 772
Dihydrodianthrone, catalyst, oxidation of petroleum, 964
Dihydronaphthalene, from disodiumnaphthalene, 958
Dihydronaphthalene, from disodiumnaphthalene, 958
—, naphthalene carboxylic acids from, 958
1,2-Dihydronaphthalene, preparation of, 906
1,4-Dihydronaphthalene, reaction with ethyl hypochlorite, 626
Dihydroxyacetone, antidote for hydrocyanic acid, 434
Dihydroxyanthraquinones, as antioxidants, 918
o-Dihydroxybenzene, from chlorobenzenes, 782
—, *see also* Pyrocatechol
Dihydroxybenzenes, stabilizers for gasoline, 917
3,4-Dihydroxy-*ter*-butylbenzene, as antioxidant, 916
Dihydroxybutyric acid, from crotonic acid, 547
1,2-Dihydroxy-4-cyclohexylbenzene, as antioxidant, 916
Dihydroxydimethylperoxide, from methane, 882
β,β′-Dihydroxyethyl sulphide, from ethylene oxide, 463
Dihydroxyfluorenes, as antioxidants, 918
Dihydroxynaphthalenes, as antioxidants, 918
1,5-Dihydroxynaphthalene, reaction with ethanolamine, 569
Dihydroxyperylenes, antioxidants, for gasoline, 918
Di-β-hydroxypropylamine, preparation of, 585
β-γ-Dihydroxypropylaniline, reaction with ethylene oxide, 561
1,2-Dihydroxy-4-propylbenzene, as antioxidant, 916
Di-iodofluoromethane, from iodoform, 737
—, reaction with ammonia, 737
Di-iodomethane, reaction with ethers, 345
Diisoamyl ketone, from isopentane, 445
Diisobutylene, decomposition of, 184
—, from isobutene, 386, 641, 642, 1300
—, hydrogenation of, free energy change, 1300
—, —, —, effect of temperature on, 1300
—, molal entropy, 1291
—, oxidation of, 895
—, pyrolysis of, 87
—, reaction with benzene, 592
—, — phenol, 604
Diisocrotyl, from diisobutylene, 87
Diisopropylamine, formation of, 428
Diisopropylbenzene, preparation of, 208, 382, 383, 402, 592
Diisopropyl ether, formation of, 363, 377, 530
—, reaction with acetic acid, 377
2,4-Diisopropylphenylisopropyl ether, preparation, 403
Diisopropyl sulphate, diisopropyl ether from, 363
—, preparation of, 305, 358, 361
—, reaction with benzene, 597, 598
—, — hydrogen peroxide, 381
Diisopropyltoluene, from toluene, 382
Diketene, preparation of, 441
—, reaction with aniline, 442
Diketones, reaction with nitroparaffins, 1096
1,3-Dimethoxybenzene, reaction with isobutene, 606
Dimethyl acetal, formation of, 714
Dimethylacetylene, preparation of, 722
β,β-Dimethylacrolein, preparation of, 444
unsym-Dimethylallene, polymerization of, 650
Dimethylamine, reaction with pentene-1,2-oxide, 589
—, promoter, esterification of *ter*-butanol, 412
1-Dimethylaminopentanol-2, preparation of, 589
Dimethylaniline, amine nitrate from, 623
—, as antiknock, 1018
—, in sulphation of alcohols, 1085
—, isoamylene from, 623
—, production of, 311
Dimethylanthracene, from toluene, 208
2,6-Dimethylanthracene, from *p*-xylene, 96
—, pyrolysis of, 96
Dimethyl-N-anthranilic acid, use in hydrogen sulphide removal, 458
2,6-Dimethylbenzoquinone, from mesitylene, 954
2,2′-Dimethylbiphenyl, from toluene, 260

Dimethyl bis (diethylmethyl) lead, preparation of, 823
1,3-Dimethylbutadiene-1,3, preparation of, 173
Dimethylbutadiene, reaction with nitrogen trioxide, 697
2,3-Dimethylbutadiene, co-polymerization with chloroprene, 681, 682
2,2-Dimethylbutane, formation of, 601
2,3-Dimethylbutane, detonation of, 1017
—, in petroleum, 32
2,2-Dimethylbutanol, from 2-methylpentene-1, 388
3,3-Dimethylbutanol-2, dehydration of, 401
Dimethylchloramine, reaction with ketene, 440
Dimethylcyclohexane, action of aluminum chloride on, 206
—, cracking of, 111
—, from ethylcyclohexane, 205
—, pyrolysis of, 93, 185
1,2-Dimethylcyclohexane, from petroleum, 34
1,3-Dimethylcyclohexane, from cyclohexane, 205
1,4-Dimethylcyclohexane, autoxidation of, 907
—, in gasoline, 144
Dimethylcyclohexanol, reaction with phosphorus pentachloride, 775
1,3-Dimethylcyclohexene, reaction with bromine, 775
Dimethylcyclopentane, in gasoline, 34
Dimethyldicyclopentyl, from cyclohexane, 205
—, from decalin, 206
1,4-Dimethyl-2,3-diethyl-1,3-butadiene, from diethylpinacone, 678
Dimethyl-*p*-dioxane, from acetaldehyde, 579
Dimethyldioxane, from propene oxide, 579
Dimethyl ditelluride, formation of, 50, 51
Dimethyl ether, catalyst, oxidation of hydrocarbons, 862
—, chlorination of, 529
—, from methyl chloride, 796
—, methyl chloride from, 794
—, reaction with benzal chloride, 794
—, — chloroform, 729
Dimethylethyl acetic acid, preparation of, 819
***unsym*-Dimethylethylene, from di-*ter*-butylethylene, 87**
Dimethylethylene, from isobutyl bromide, 806
***a*-Dimethyl-ethylene chlorohydrin, preparation of, 520**
Dimethyl glycolic aldehyde, from 2-butene, 897
Dimethyl glyoxal, from 2-butene, 897
3,3-Dimethylheptane, in shale oil, 33
2,5-Dimethylhexane, pyrolysis of, 72
—, *p*-xylene from, 73
Dimethyl-*n*-hexylcarbinol, preparation of, 450
4,4-Dimethyl-3-isopropylbutene-2, formation of, 411
Dimethylketoxime, from propyl pseudonitrole, 1094
Dimethylmorpholine, preparation of, 585
Dimethyl mercury, formation of, 50
—, reaction with mercuric bromide, 51
Dimethylnitrosoamine, in fuels, 1098
2,7-Dimethyloctane, *m*-methylisopropylbenzene from, 73
—, nitration of, 1090
2,7-Dimethyloctene, preparation of, 807
2,2-Dimethylpentane, from petroleum, 32
4,4-Dimethylpentanol-2, dehydration of, 400
3,4-Dimethylpentan-2-one, *see* Methylisopropylacetone
3,3-Dimethyl-1-pentene, from carbon monoxide and hydrogen, 1243
4,4-Dimethylpentene-1, preparation of, 400
—, reaction with hydrogen bromide, 318
4,4-Dimethylpentene-2, preparation of, 400
Dimethylpentenol, reaction with hypochlorous acid, 521, 522
Dimethyl phthalate, decarboxylation of, 952
—, methyl benzoate from, 952
1,2-Dimethyl-1,3-propanediol, from 2-butene, 624
1,2-Dimethylpropanol-1, dehydration of, 400
Dimethylquinoline, from anthracene oil, 839
—, from petroleum, 834, 838
Dimethyl sulphide, in petroleum, 454
1,1′-Dinaphthyl, perylene from, 208
2,2′-Dinaphthyl, from naphthalene, 208
—, perylene from, 209
Dinaphthylene oxides, as antioxidants, 918
Dinaphthyl ethers, formation of, 500
Dinitrate, from tetramethylethylene, 621, 622
Dinitrite, from tetramethylethylene, 621
***m*-Dinitrobenzene, extraction with butanone, 1148**
1,1,1-Dinitrochloroethane, formation of, 451
4,6-Dinitro-3-ethyloltoluidine, preparation of, 570
Dinitrotetramethylethane, preparation of, 621
Dinitrotoluene, separation from trinitrotoluene, 496
Diolefins, absorption by cuprous chloride, 391
—, adsorption of, 255
—, condensation with acid anhydrides, 687-690
—, — acids, 688, 690, 691
—, — aryl halides, 691
—, — maleic anhydride, 679
—, — quinones, 175, 679, 688, 689
—, dicarboxylic acids from, 698
—, effect of pressure on, 666
—, — lead tetraethyl on, 1019, 1020
—, effect on gasoline, 909
—, estimation, 698-700
—, halogenation, 683, 690, 700
—, in gasoline, 913
—, oxidation of, 666
—, polymerization of, 88, 170, 310, 385, 649-654
—, pyrolysis of, 88
—, reaction with alkali metals and amines, 698
—, — diazotized aniline, 700
—, — formic acid, 698
—, — halogen acids, 699
—, — mesityl oxide, 175
—, — sulphur chloride and oxygen, 696
—, — sulphur dioxide, 176
—, reduction to monolefins, 698
—, removal from gaseous mixtures, 359
—, separation from amylenes, 310
—, solvent action of dioxane on, 581
—, use in peroxidation, 923
Diols, dehydration of, 548
Dioxane, chlorination of, 581
—, oxidation of, 580
—, pharmacological properties of, 580
—, preparation of, 551, 578, 579
—, pyrolysis of, 580
—, reaction with arsenic trichloride, 580
—, solvent power of, 580
—, utilization of, 581
1,3-Dioxolane, preparation of, 582
Dioxalanes, from alkylacetylenes, 724
Dioxalones, from alkylacetylenes, 724
Dipentene, reaction with formaldehyde, 624
—, — selenious acid, 446
Diphenylamines, as antioxidants, 940
—, as heat-transfer medium, 194
—, from benzene, 260
—, from bromobenzene, 787
—, from phenyl chloride, 810
—, in esterification of olefins, 316, 318
***p*-Diphenylbenzene, from benzene, 95**
Diphenylbutadiene, formation of, 649
Diphenylcyclohexane, from benzene, 207
Diphenyl dinitroethane, from stilbene, 621
γ,γ′-Diphenyldipropyl ether, preparation of, 529
Diphenylene ditelluride, as antiknock, 1018
Diphenylene oxide, reaction with chlorinated paraffins, 758
1,2-Diphenylethane, from toluene, 260
Diphenyl ether, as heat-transfer medium, 861
—, from phenol, 788, 789
—, from potassium phenolate-ethylene chloride reaction, 500
—, in dehydrogenation of alcohols, 420
—, in high-temperature lubricant, 194
—, reaction with chlorinated paraffin, 818
Di-β-phenylethyl ether, preparation of, 529
Diphenylguanidine, adsorption by carbon black, 252
—, accelerator, production of carbon black, 239
Dipole moment, definition of, 441
Diphenylmethane, benzophenone from, 943, 957
—, in dehydrogenation of alcohols, 420
—, molal entropy, 1289
—, oxidation of, 943, 957
Diphenyl oxide, as heat-transfer agent, 860
Diphenyl sulphide, from benzene, 468

Dipropenyl, from diallyl, 88
Dipropyl ketone, decomposition of, 450
—, ethyl dipropyl carbinol from, 452
—, photochemical decomposition, 449
—, preparation of, 443
—, solvent, 443
Dipropyl ether, dewaxing agent, 495
Disodium glycolate, dehydrating agents, 330
Disodium naphthalene, dihydronaphthalene from, 958
Disodium phosphate, in fermentation of sucrose, 547
Disodium thioglycolate, in olefin estimation, 1144
Dispersing agents, by sulphonation of ethers, 825
—, — oxygenated hydrocarbons, 1061
—, ethanolamine salts as, 575
—, ethylene oxide in preparation of, 566
—, for graphite, 576
—, from mercaptans, 472
—, hydroxyethyl ethers as, 558
—, naphthenic acids in, 1112, 1117
—, naphthenic alcohols as, 1120
—, sulphuric acid esters in, 1112
—, urethans as, 569
Disulphides, antioxidants, for white oils, 937
—, effect on color stability, 454, 456
—, — lead susceptibility, 456, 480, 481, 1031
—, from alkyl sulphur chlorides, 478
—, from mercaptans, 470, 471, 480
—, in insecticides, 1112
—, in petroleum, 454
—, reaction with ammonia and sulphur, 481
Disulpho-butyric acid, formation of, 616
Disulphonic acids, catalyst, esterification of acetylene, 717
Disulpho-propionic acid, formation of, 616, 820
1,3-Dithiane, preparation of, 485
1,4-Dithiocyanobutene, chlorination of, 698
—, from butadiene, 698
Dithionic acid, catalyst, dehydration of alcohols, 410
—, —, hydration of higher olefins, 297, 410
Ditolyl, from toluene, 208
Ditolyl disulphide, flotation agent, 486
Ditolylethane, formation of, 719
Ditolyl mercury, as antioxidant, 938
Divinylacetylene, hydration of, 709
—, hydrogenation of, 709
—, polymerization of, 708, 709
—, preparation of, 704, 708
—, reaction with chlorine, 709
—, — hydrogen polysulphide, 709
—, — thio-*p*-cresol, 709
Divinyl ether, from *β,β'*-dichloroethyl ether, 528
—, from acetylene, 715
—, in anesthesia, 528, 529
—, reaction with acetyl iodide, 612
Dixylylethane, preparation of, 719
Doctor solution, estimation of sulphur, 1156, 1157
Doctor sweetening, defined, 474
Dodecane, from *n*-tetradecane, 1297
Dodecene, from 1-hexene, 1299, 1300
—, from isobutene, 643
—, from propene, 639
—, in kerosene, 145
—, reaction with benzene, 591
n-Dodecyl ammonium thiosulphate, preparation of, 829
Dodecylbenzene, preparation of, 1254
Dodecyl chloride, reaction with sodium thiocyanate, 822
Dodecyl halides, glycol ethers from, 543
n-Dodecyl iodide, reaction with ammonium thiosulphate, 829
Dodecyl mercaptan, reaction with ethylene oxide, 564
Dodecyl thiocyanate, use as insecticide, 822
a-Dodecylthiol, reaction with ethylene chlorohydrin, 526
Driers, fatty acids in, 1115
—, from lead tetra-alkyls, 823
—, from naphthenic acids, 1115
—, from sulphonates, 1081
—, from wax acids, 1055
Drying oils, acetylene in synthesis of, 701
—, by oxidation of petroleum, 1054, 1055
—, from copolymerization of olefins and diolefins, 203
—, from acid sludge, 1055
Dubbs process, of cracking, 117
Dubrovai process, of cracking, 123, 124
Ductility, of asphalts, 1207, 1208
Duo-Sol process, 43
Duprene, definition of, 681
—, *see* Neoprene
Durene, from xylenes, 208
Dust fixatives, preparation of, 1079
Dyes, estimation of benzene with, 1185
—, from chlorobenzenes, 782
—, oil-soluble, preparation of, 1079
—, phthalic anhydride in, 946
—, sulphonated naphthenic acids as, 1117, 1118
—, water-soluble, oil-soluble from, 1079
Dyestuffs, antioxidants for gasoline, 919
—, inhibitors, gum formation, 913

E

Earthenware fragments, catalyst, in Houdry process, 129
Edeleanu extract, for dehydration of isopropyl alcohol, 364
Electric discharge, action on alcohols, 256, 262
—, — esters, 262
—, — gaseous hydrocarbons, 253, 254
—, — kerosene, 253
—, — petroleum hydrocarbons, 255, 256, 262
—, — water, 256
—, ignition, 1001, 1002
—, polymerization by, 631
Electrion oils, preparation of, 260-263
Electrodes, use in cracking methane, 54
Electrolytic chlorination, of benzene, 780
Electromagnetic field, action on acetylene, 267
—, — gasoline, 267, 268
Electromotive force, free energy change from, 1276, 1277
Emulsifiers, natural, in crude petroleum, 1217
Emulsifying agents, alkyl thiosulphates as, 828, 829
—, by sulphonation of ethers, 825
—, calcium sulphonate as, 1074
—, ethanolamine salts as, 575, 1074
—, ethylene glycol ethers as, 543, 558
—, ethylene glycol in, 1114
—, ethylene oxide in preparation of, 566
—, for asphalts, 1216, 1217, 1218
—, formaldehyde in, 891
—, from chlorinated hydrocarbons, 758, 822
—, from ethylene chlorohydrin, 526
—, from mercaptans, 472, 487
—, from petroleum, 1060
—, from tertiary alcohols, 417
—, humic acids used as, 1099
—, kaolin in, 1074
—, mineral oil in, 1079
—, naphthenic acids in, 1112
—, naphthenic acid soaps as, 1114
—, naphthenic alcohols as, 1120
—, polyhydric alcohols in, 1074
—, rosin in, 1114
—, rosin soaps in, 1079
—, sulphates as, 1085, 1086
—, sulphonaphthenic acids as, 1118
—, sulphonated castor oil in, 1074
—, sulphonic acids as, 1074, 1075, 1079
—, sulphuric acid esters in, 1112
—, wax acids as, 978
Emulsions, aquolysis of, 133
—, breaking of, 10, 757, 946, 947
—, in crude oil, 10
—, stabilizers for, 584
Enamels, preparation of, 728
Endothermic reactions, in cracking process, 103
Energy, of activation, dehydrogenation of cyclohexane, 92
—, —, of cracked naphtha, 102
—, —, of halogen-olefin reactions, 491

Energy, of activation, of mazout, 103
—, —, of petroleum fractions, 102
—, —, of propane, 58
—, —, pyrolysis of benzene, 95
Enthalpy, definition of, 1306
—, *see also* Heat content
Enthalpy diagrams, determination of, 1332-1335
Enthalpy-pressure-temperature relations, of benzene, 1333
—, of crude oil, 1334, 1335
—, of naphtha, 1333, 1334
—, of *n*-pentane, 1333, 1334
Enthalpy table, for methane, 1337
Entropy, definition of, 1273-1275, 1306
—, molal, of acetylene, 1282-1284
—, —, of aromatics, 1289, 1290
—, —, of isoparaffins, 1281, 1282, 1288, 1289, 1292, 1293
—, —, of naphthenes, 1284-1286, 1290
—, —, of olefins, 1282-1284, 1290, 1291
—, —, of palmitic acid, 1292, 1293
—, —, of *n*-paraffins, 1279, 1280, 1281, 1288, 1289
—, —, of 1,4-pentadiene, 1291
—, of formation, of acetylene, 1282-1284
—, —, of aromatics, 1284-1286
—, —, of cyclohexene, 1284, 1285
—, —, of naphthenes, 1284-1286
—, —, of olefins, 1282-1284
—, —, of *n*-paraffins, 1279, 1280, 1281
—, of fusion, definition of, 1288
—, relation to free energy, 1275
—, — equilibrium constant, 50
—, — heat capacity, 1273, 1306
—, — heat of reaction, 50
Entropy change, effect of structure on, 1286, 1288-1293
—, evaluation from heat capacity, 1278, 1279
—, — from specific heat, 1277
—, free energy change from, 1276, 1277
—, isomerization *n*-butane to isobutane, 1282
Entropy chart, of dichloromethane, 1337
Entropy-heat content relations, 1341-1343
Entropy table, for methane, 1337
Entropy-temperature relations, 1335-1341
Entropy units, definition of, 1280
Eosin, catalyst, cyclohexene-oxygen reaction, 898
Epichlorohydrin, preparation of, 523
—, uses of, 524
Epinephrine, effect on heart, 1269
Eponit-Ratibor, to clarify wines, 232
1,8-Epoxynaphthalene, as antioxidant, 918
Equations of state, 1319
Equilibrium constant, free energy change from, 1276, 1277
—, relation to free energy change, 50, 1275, 1276
—, — entropy, 50
Esters, action of electric discharges on, 262
—, by oxidation of petroleum, 962, 963
—, from aldehydes, 889
—, from carbon monoxide and hydrogen, 1223
—, from paraffin wax, 971, 972
—, from wax acids, 970
—, halogenated, reaction with olefins, 613, 614
—, in co-polymerization of chloroprene, 681, 682
—, pyrolysis of, 341
—, solvents for asphalts, 1202
Esterification, of alcohols, 1080, 1081, 1118-1120
—, of ethylene glycol, 540, 541
—, of phthalic anhydride, 541
—, of polyglycols, 545
—, of polyhydric alcohols, 541
—, of polymethylene alcohols, 1118, 1119
—, of wax acids, 975
Ethane, acetic acid from, 856, 857, 858
—, acetylene from, 168
—, acids from, 871, 872
—, action of glow discharge on, 257
—, — silent discharge on, 257
—, alcohols from, 857, 858, 871, 872
—, aldehydes from, 856-858, 871, 872
—, analysis of, 1130, 1131
—, and propane, extraction agent, 42
—, as motor fuel, 1040
Ethane, bromination of, 747
—, carbonization of, 56
—, chlorinated, properties of, 743
—, —, uses for, 744, 745
—, chlorination of, 741
—, combustion of, 52
—, depressant, decomposition of ethylene oxide, 554
—, effect on viscosity of crystal oil, 15
—, entropy-temperature relations, 1336, 1339
—, ethyl alcohol from, 856, 857, 858
—, ethylene from, 151
—, —, free energy change, 1284
—, fluorinated, properties of, 748, 749
—, fluorination of, 747
—, formaldehyde from, 856, 857
—, formic acid from, 856, 857, 858
—, free energy of formation, 1225
—, —, effect of temperature on, 1294
—, from butane, 62, 64, 201
—, from carbon monoxide and hydrogen, 1226, 1241, 1242
—, from cracking gas, 301
—, from cracking operations, 140
—, from cyclohexane, 93
—, from cyclopentane, 90
—, from ethyl alcohol, 331, 350, 357
—, from ethylene oxide, 554
—, from free radicals, 53
—, from gas oil, 140
—, from *n*-hexane, 71
—, from methane, 158, 257
—, from methyl ethyl ketone, 449
—, from methyl propyl ketone, 450
—, from natural gases, 22
—, from *n*-nonane, 72
—, from *n*-pentane, 68
—, from pentene, 86
—, from propene, 80
—, from toluene, 260
—, heat of combustion, 15
—, ignition of, 1001
—, ignition temperature of, 987, 988, 989, 992, 993
—, inflammability limits of, 984
—, in petroleum gases, 21
—, methyl alcohol from, 856, 857, 858
—, Mollier diagram, 1341-1343
—, nitration of, 1087
—, oxidation of, 846-848, 850, 856-858, 869, 871-873, 1129, 1130
—, pyrolysis of, 55, 56, 148-150, 151, 158
—, resins from, 257, 258
—, separation from ethylene, 1140
Ethane-acetylene, azeotropic mixture of, 1140
Ethane bromides, hydrolysis of, 805
Ethane chlorides, narcotic effect of, 745
—, as dry cleaning agents, 745
—, as refrigerants, 745
—, in insecticides, 745
—, in refining lubricants, 744, 745
sym-Ethane disulphonic acid, from nitroethane, 1096
Ethanethiol, reaction with ketene, 438
Ethanol, *see* Ethyl alcohol
Ethanolamine, catalyst, reaction of alcohols and alkene oxides, 568
—, —, — ethylene dichloride and sodium polysulphide, 499
—, condensation of, 568
—, dehydrogenation of, 568
—, dispersing agent, 576
—, from ethylene oxide, 567
—, reactions of, 568, 569
Ethanolamines, absorption of carbon dioxide, 573, 574
—, as reducing agents, 570
—, decomposition of, 570
—, in soaps, 575
—, inhibitors, gum formation, 915
—, reaction with metallic salts, 570
—, — phthalic anhydride, 958
—, — thionyl chloride, 570
—, removal of sulphur from gases, 573, 574
—, sulphuric esters of, uses, 578
Ethanolamine salts, uses, 575

Ether, effect on leucocytosis, 1268
—, flocculating agent for asphalts, 1196
—, fractional extraction of mazout with, 1188
—, from propene, 358
—, purification of, 336
Ether, *see also* Diethyl ether
Ether peroxides, catalysts, reaction of ethylene and sulphur dioxide, 617
Ethers, aliphatic, reaction with acetyl iodide, 611
—, antioxidants for gasoline, 916
—, extractants for asphalts, 1187, 1202
—, formation during olefin hydration, 283
—, from acetals, 715
—, from alcoholates, 825
—, from alcohols, 406, 413, 579
—, from alcohol-vinylacetylene reaction, 705
—, from alkyl halides, 804, 825
—, from chlorohydrins, 524, 525
—, from esters, 406
—, from olefins, 331, 406
—, peroxides from, 380, 381
—, reaction with alcohols, 715
—, — alkyl halides, 345
—, rearrangement of, rules for, 825, 826
—, solubilities of, in sulphuric acid, 379
Ethionic acid, from ethylene, 321, 1082
4-Ethoxy-2-butyne, reaction with ethyl alcohol, 705
2-Ethoxy-1,1-dimethylethanol, from isobutene oxide, 548
2-Ethoxyethanol, reaction with ketene, 435
2-Ethoxyethyl acetate, preparation of, 435
2-Ethoxyethyl caprylate, as plasticizer, 543, 544
5-Ethoxymorpholine, preparation of, 561
Ethyl acetate, estimation of paraffin wax, 1155
—, from ethyl alcohol, 337, 341, 421
—, from ethylene, 304, 305
—, in stabilizing carbon tetrachloride, 730
—, precipitant for asphaltenes, 1192
—, pyrolysis of, 341, 421, 423
Ethyl acetoacetate, reaction with acetylene, 721
p-Ethylacetophenone, from benzene, 439
Ethylacetylene, from methylallene, 88
—, reaction with acetic acid, 718
Ethyl alcohol, absorbent for butadiene, 174
—, acetal from, 339
—, acetaldehyde from, 337-340, 348, 349, 844, 878, 879
—, acetic acid from, 338, 339, 421, 844
—, acetone from, 340, 421, 422
—, acetone in, 327
—, activity in sulphuric acid, 343, 344
—, aromatics from, 342
—, as antiknock, 1016, 1017
—, as chemical intermediate, 330
—, azeotropic distillation of, 328, 329
—, azeotropic mixture with isopropyl alcohol, 369
—, *n*-butanol from, 337
—, butyl acetate from, 338
—, by fermentation, 319
—, catalyst, reaction of ethylene dichloride and ammonia, 497
—, combustion of, 1004, 1005
—, dehydration of, 328, 329, 330, 1051
—, dehydrogenation of, 288, 337, 348, 878
—, diamyl ether from, 337
—, dibutyl ether from, 337
—, diethyl ether from, 330, 331, 332
—, electrical decomposition of 256, 347
—, estimation of, 353, 354, 355
—, estimation of paraffin wax, 1155
—, 2-ethoxy-1,1-dimethylethanol from, 548
—, ethyl acetate from, 337-341, 421
—, ethyl hypochlorite from, 626
—, ethylsulphuric acid from 343
—, ethyl xanthate from, 355
—, explosive characteristics of, 1011
—, extraction agent for asphalts, 1188, 1200
—, — diolefin bromides, 1144
—, — petroleum sulphonates, 1070, 1071
—, — yellow zein, 496
—, flash point of, 988
—, formaldehyde from, 337, 879
Ethyl alcohol, from carbon monoxide and hydrogen, 319, 1305
—, —, free energy change, 1305
— from diethyl sulphate, 326, 327
—, from ethane, 856-858, 872
—, from ether, 332, 333, 334, 421
—, from ethyl acetate, 421
—, from ethylene, 282-291, 319, 322, 323, 552
—, —, free energy change, 1302, 1303
—, from ethylsulphuric acid, 326, 327
—, from hydrocarbons and steam, 269
—, from pentane, 859
—, gels with, 330
—, hexanol from, 341, 347
—, hydrogenating agent, 347
—, hydrogen from, 339-341, 347, 348, 352
—, in anti-freeze mixtures, 374
—, in coating compositions, 353
—, in demulsifying agents, 1075
—, inflammability limits of, 980, 981, 982
—, in fuels, 319, 330
—, inhibitor, dechlorination of tetrachloroethane, 805
—, in insecticides, 790
—, in rubber cement, 374
—, octane number of, 1028
—, oxidation of, 844, 872, 879, 880
—, pentanol from, 347
—, propionic acid from, 339
—, pyrolysis of, 155, 173, 331, 339-342, 347-353, 551
—, reaction with acetone, 443
—, — alkali hydroxides, 342
—, — alkali metals, 342
—, — aluminum, 342, 343
—, — amines, 346, 347
—, — carbon monoxide, 339
—, — chlorine, 626
—, — chlorine and cinnamic acid, 627
—, — 4-ethoxy-2-butyne, 705
—, — ethylsulphuric acid, 332
—, — hydrogen chloride, 345, 742
—, — ketone cyanohydrin, 451
—, — piperidine, 346
—, — platinic chloride, 628
—, — sodium phenolate and carbon monoxide, 957
—, — sulphuric acid, 343
—, — trichloroacetyl glycols, 541
—, — vinylacetylene, 706
—, — zinc sulphate, 878
—, refining montan wax with, 353
—, sodium acetate from, 342
—, solvent properties of, 319, 353, 568, 681
—, to convert gels into sols, 560
—, toluene from, 173
Ethyl alcohol-gasoline, blends, as motor fuel, 1034-1038
Ethylamine, reaction with dibiphenylene ethylene, 615
Ethylaniline, preparation of, 346
—, reaction with butadiene and lithium, 698
Ethyl atropate, preparation of, 451
Ethylbenzene, action of aluminum chloride on, 208
—, benzene from, 96, 208
—, diethylbenzene from, 208
—, effect of lead tetraethyl on, 1022
—, from benzene, 206, 207
—, from *n*-octane, 73
—, from toluene, 208
—, from vinylcyclohexane, 93
—, hydrogen from, 96
—, in petroleum, 34
—, methane from, 96
—, molal entropy, 1289
—, naphthalene from, 96
—, olefins from, 96
—, oxidation of, 942, 943
—, pyrolysis of, 95, 96, 156, 159
—, reaction with acetylene, 719
—, styrene from, 96, 159
—, toluene from, 96
—, triethylbenzene, from, 208
Ethyl benzoate, from diethyl phthalate, 952

Ethyl blending chart, definition of, 1031
Ethyl bromide, catalyst, for Grignard reaction, 772
—, from ethyl alcohol, 345.
—, from ethylene, 304
—, reaction with mercuric fluoride, 748
Ethyl *n*-butyl ketone, preparation of, 589
Ethyl butyrate, use in dewaxing, 353
Ethylcellulose, preparation of, 745
Ethyl chloride, dechlorination of, 805
—, dehydration agent for isopropyl alcohol, 364
—, dewaxing agent for lubricating oils, 738, 739
—, estimation of, 744
—, from ethyl alcohol, 345, 742
—, from ethylene, 301, 302, 304, 305, 742
—, from still gases, 741
—, hydrolysis of, 796, 797
—, in insecticides, 745
—, in refrigerants, 745
—, purification of, 303
—, reaction with ammonia, 808
—, — aniline, 808
—, — cellulose, 745
—, — *α*-naphthylamine, 808
—, — sorbitol, 826
—, — *o*-toluidine, 808
Ethyl chlorosulphinate, preparation of, 346
Ethyl chlorosulphonate, catalyst, reaction of ethylene and hydrogen chloride, 301
Ethyl cyanide, in stabilizing carbon tetrachloride, 730, 731
Ethylcyclohexane, benzene from, 93
—, butadiene from, 93
—, dimethylcyclohexane from, 205, 206
—, from petroleum, 31, 34
—, from styrene, 1154
—, from vinylcyclohexane, 93
—, hydrogen from, 93
—, isomerization of, 205, 206
—, methane from, 93
—, pyrolysis of, 91, 93
—, toluene from, 93
trans-2-Ethylcyclohexanol, preparation of, 589
2-Ethylcyclohexene, oxidation of, 900
Ethylcyclohexyl malonate, preparation of, 773
Ethyldipropyl carbinol, preparation of, 452
Ethylene, absorption by *ter*-butyl hypochlorite, 627
—, — body, 1267
—, — cuprous salts, 163, 164
—, acetic acid from, 629
—, acetylene from, 79, 160, 166, 167
—, action of silent discharge on, 258
—, adsorption by carbon, 324
—, anthracene from, 77, 186
—, as anesthetic, 1256-1261
—, as motor fuel, 1040
—, benzene from, 77, 186
—, butadiene from, 78, 172, 258, 637
—, butene from, 258, 636, 639
—, carbon monoxide from, 622
—, carbyl sulphate from 321, 1081, 1082
—, combustion of, 52, 241, 1001, 1003-1005, 1010
—, dichlorodiethyl sulphide from, 619
—, diethyl sulphate from, 321
—, esterification of, 304, 305, 359
—, estimation of, 1141, 1142, 1259
—, ethionic acid from, 321, 1082
—, ethyl alcohol from, 322, 323
—, —, free energy change, 1302, 1303
—, ethylene glycol from, 627
—, ethylene glycol dinitrate from, 621
—, ethylene glycol molybdate from, 628
—, ethylene glycol nitrate nitrite from, 622
—, ethyl ether from, 322, 323
—, ethylsulphuric acid from, 321, 322
—, explosive properties, 77, 1257, 1258
—, from acetylene, 719
—, from allyltoluene, 96
—, from benzene, 207
—, from *n*-butane, 62-64
—, from carbon dioxide and hydrogen, 1241
—, from carbon monoxide and hydrogen, 1223, 1241
—, from chlorocyclohexene, 172
—, from cracked tar, 155
Ethylene, from cracking gas, 301, 302
—, from cyclohexane, 92, 93, 185
—, from cyclopentane, 90
—, from dibromoethane, 805
—, from ethane, 56, 57, 151
—, —, free energy change, 1284
—, from ether, 334
—, from ethyl acetate, 421
—, from ethyl alcohol, 155, 173, 331, 340, 551
—, from ethylidene bromide, 805
—, from gas oil, 140
—, from gasoline, 136
—, from heptane, 71, 154
—, from isobutane, 67
—, from isobutene, 85
—, from kerosene, 154, 155, 253
—, from ketene, 437
—, from ketones, 449, 450
—, from Kogasin II, 155
—, from methane, 53, 54, 158, 166, 218, 257
—, from 1-methylcyclohexene, 172
—, from methylene radicals, 53, 438
—, from oils, 131
—, from paraffin wax, 138
—, from peat tar, 155
—, from *n*-pentane, 68
—, from pentenes, 86
—, from petroleum hydrocarbons, 253, 254
—, from potassium ethylene trichloroplatinate monohydrate, 628
—, from propane, 58-61, 80, 149, 151, 153, 169
—, from *n*-propyl alcohol, 173
—, from tetrahydrobenzene, 93
—, from toluene, 260
—, from vinyl radical, 75
—, hexene-1 from, 258
—, hydration of, 282-291
—, —, free energy change, 283, 284, 290, 1302, 1303
—, —, —, effect of temperature on, 1302, 1303
—, —, heat, 287
—, hydrogen from, 79
—, ignition temperature of, 987-989
—, inflammability limits of, 980, 985
—, in heat-transfer media, 539
—, inhibitor, decomposition of ketene, 437
—, —, pentane-chlorine reaction, 493
—, in pressure-transfer media, 539
—, iodoalkyl nitrate from, 629
—, isobutane from, 637
—, lubricating oil from, 210
—, naphthalene from, 77, 186
—, *α*-nitroethyl nitrate from, 622
—, oxalic acid from, 622
—, oxidation of, 551, 844, 851, 894, 896, 897
—, —, effect of temperature on, 849
—, —, mechanism, 847, 848, 896
—, pentene from, 639
—, physiological properties, 1257, 1260-1262, 1268, 1269
—, polymerization of, 202, 203, 209, 210, 265, 283, 288, 290, 321, 634, 636-639, 646, 671
—, —, effect of hydrogen, 166
—, —, effect of pressure, 638, 639, 1041
—, pressure-volume-temperature relations, 1322
—, propene from, 636, 639
—, propionic acid from, 446, 626
—, pyrolysis of, 77-79, 166, 184
—, reaction with acetyl chloride, 611, 612
—, — benzene, 594, 595, 597
—, — bromine, 501
—, — butadiene, 186
—, — *ter*-butyl hypochlorite, 518
—, — carbon monoxide, 626, 893
—, — chlorine, 492-494
—, — chloromethyl acetate, 613
—, — N-chlorourea, 515, 516
—, — coal-tar distillates, 209, 593
—, — cracked gas, 1252, 1253
—, — cracked gasoline, 1252, 1253
—, — cyclohexane, 601, 602
—, — ethylene chlorohydrin, 529
—, — ethylsulphuric acid, 298
—, — with halogen acids, 300

Ethylene, reaction with hydrogen chloride molybdic anhydride complex, 628
—, — hydrogen peroxide, 897
—, — hypochlorous acid, 515-520
—, — iodine, 505
—, — isobutane, 599, 601
—, — isopentane, 599
—, — mercuric nitrate and iodine, 629
—, — metal hydroxide, 894
—, — methylcyclohexane, 599
—, — methylcyclopentane, 599
—, — naphthalene, 209, 210, 594
—, — nitric acid, 622
—, — nitrogen tetroxide, 620
—, — oxygen and water, 534
—, — phenol, 605
—, — phosgene, 609, 611
—, — phosphoric acid, 323
—, — potassium hydroxide, 629
—, — propane, 601
—, — steam, 271
—, — stearic acid, 588
—, — sulphur chloride and sodium polysulphide, 618, 619
—, — sulphur dioxide, 617
—, — sulphur mònochloride, 619
—, reaction with sulphuric acid, 161, 298, 319-325, 343, 344, 391, 1081, 1082, 1141, 1142
—, —, effect of concentration, 321
—, —, effect of pressure, 321, 322
—, —, effect of temperature, 321
—, reaction with tetralin, 209
—, — 2,2,4-trimethylpentane, 599
—, removal from gas mixtures, 161-164, 327, 328
—, resins from, 618, 619
—, separation from ethane, 1140
—, — propene, 163
—, sulphinic esters from, 617
—, sulphones from, 617
—, tars from, 656
—, toluene from, 77, 186
—, xylene from, 186
Ethylene-aluminum chloride, catalyst, polymerization of cracked distillates, 214
Ethylene bromide, *see* Ethylene dibromide
Ethylene bromohydrin, ethylene glycol from, 532
—, from ethylene oxide, 565
—, reaction with carbon dioxide, 532
Ethylene chloride, *see* Ethylene dichloride
Ethylene chlorohydrin, acrylic acid from, 527
—, as insecticide, 519
—, β,β′-dichloroethyl ether from, 528
—, effect on plant growth, 519
—, ethylene glycol from, 532
—, ethylene oxide from, 550
—, extraction agent for butadiene, 174
—, from ethylene, 515-520
—, from ethylene dichloride, 517, 518
—, from ethylene glycol, 537
—, from ethylene glycol diacetate, 518
—, from ethylene oxide, 516, 560
—, β-haloethylarsines from, 526
—, hydrolysis of, 518, 519, 533
—, polysulphides from, 526
—, properties of, 519
—, reaction with amines, 527
—, — carbon dioxide and sodium hydroxide, 532
—, — mercaptans, 526
—, — methylol urea, 525, 526
—, — olefins and chlorine, 529
—, — resorcinol, 525
—, — sodium carbonate, 533, 534
—, — thionyl chloride, 525
—, — urea, 525
—, refining petroleum oils with, 519
—, — rosin with, 519
Ethylenediamine, as antiknock, 498
—, corrosion inhibitor, 809
—, desulphurizing agent, 458, 488
—, from ethylene dichloride, 497, 808
—, plasticizing agent for cellulose acetate, 498
—, properties of, 809
—, reaction with zinc chloride, 497
—, — zinc oxide, 497
Ethylenediamine hydrogen chloride, preparation of, 497
Ethylene diarsonic acid, barium salt, preparation of, 505
Ethylene dibromide, crystalline forms of, 730
—, ethylene glycol from, 532
—, from ethylene, 501-505
—, in fire extinguishers, 505
—, promoter, ethylene-bromine reaction, 503
—, reaction with arsenious oxide, 505
—, — carbon dioxide, 532
—, — magnesium, 505, 824
—, — potassium carbonate, 532
—, — potassium phenolate, 505
—, — sodium hydroxide, 532
—, vinyl bromide from, 504, 533
Ethylene dichloride, acetaldehyde from, 533
—, acetylene from, 497
—, azeotropic mixture with water, 500
—, crystalline form of, 730
—, dehydration agent for aliphatic acids, 501, 745
—, — butyl phthalate, 501
—, — isopropyl alcohol, 364
—, dewaxing agent for lubricants, 434, 495
—, ethylene chlorohydrin from, 517, 518
—, ethylene glycol from, 496, 532
—, ethylene glycol diacetate from, 496
—, extraction agent for polymerized hydrocarbons, 397
—, — tetryl, 496
—, — trinitrotoluene, 496
—, — white zein, 496
—, from ethylene, 492-495
—, from ethylene glycol, 537
—, hydrolysis of, 533
—, in acetylation of cellulose, 496
—, in cleaning compositions, 732, 745
—, in dielectrics, 789
—, in fumigants, 566
—, in insecticides, 496
—, in lubricating greases, 496
—, in water-proofing compositions, 496
—, motor fuel from, 501
—, properties of, 495
—, pyrolysis of, 497, 716
—, reaction with acids, 499
—, — alkalies, 496
—, — ammonia, 497
—, — barium carbonate, 533
—, — benzene, 815
—, — calcium carbonate, 533
—, — calcium sulphide, 499
—, — carbon dioxide and sodium hydroxide, 532
—, — chlorine, 501, 742
—, — phenylmagnesium chloride, 565
—, — potassium hydrosulphide, 471
—, — potassium phenolate, 500
—, — sodium acetate, 499
—, — sodium acid carbonate, 532
—, — sodium carbonate, 532, 533
—, — sodium β-naphtholate, 500
—, — sodium phenolate, 825
—, — sodium polysulphide, 499
—, — sodium stearate, 499
—, — sodium sulphide, 499
—, — sodium thiosulphate, 829
—, — sulphur trioxide, 517, 518
—, resins from, 499
—, *see also* Dichloroethane
—, solvent properties of, 495
—, toxicity of, 495
—, vinyl chloride from, 496
Ethylene dihalides, ethylene glycol esters from, 540
Ethylene di-iodide, from ethylene, 505, 506
Ethylene disulphide, from ethylene dichloride, 499
Ethylene glycol, aldehydes from, 536
—, dehydration agent for diethyl ether, 538
—, diethers from, 889
—, diethylene glycol from, 544
—, electrolyte in batteries, 539
—, estimation of, 537
—, ethylene chlorohydrin from, 537
—, ethylene dichloride from, 537
—, ethylene glycol monoacetate from, 540

Ethylene glycol, ethylene oxide from, 537
—, extraction agent for butadiene, 174
—, — calcium stearate, 789
—, from ethylene, 627
—, from ethylene dibromide, 532
—, from ethylene dichloride, 496, 499, 532, 797
—, from ethylene halohydrins, 532
—, from ethylene oxide, 557
—, hydroxyaldehyde from, 536
—, in antifreeze mixtures, 538, 539
—, in brake fluid mixtures, 539, 1114
—, in emulsifying agents, 1114
—, in heat transfer media, 539
—, in mineral oils, 538
—, in preservatives, 538
—, oxidation of, 536
—, properties of, 535-537
—, reaction with acetic acid, 540
—, — acid anhydrides, 540
—, — aldehydes, 889
—, — benzyl chloride and sodium hydroxide, 543
—, — bone grease, 540
—, — ethylene oxide, 544
—, — hydrochloric acid, 537
—, — isobutene, 544
—, — 2-methylbutene-2, 544
—, — *ter*-olefins, 414
—, — paraformaldehyde, 582
—, — phthalic anhydride, 541
—, — potassium dichromate, 537
—, solvent properties, 538
—, toxicity of, 537, 538
—, viscosity depressant for nitrocellulose, 538
Ethylene glycol acetate, as extraction agent, 44
—, from ethylene glycol, 540
—, from ethylene oxide, 540
—, in brake fluid mixtures, 540
Ethylene glycol butyl ether, plasticizers from, 542
—, in cleaning agents, 543
—, in mineral oil, 543
Ethylene glycol carbonate, preparation of, 524
Ethylene glycol diacetate, acetic anhydride from, 540
—, chlorohydrin from, 518
—, from ethylene glycol, 540
Ethylene glycol dinitrate, from ethylene, 621, 622
—, in explosives, 539
Ethylene glycol distearate, preparation of, 499
Ethylene glycol esters, acid anhydrides from, 540
—, from epoxides, 540
—, from ethylene dihalides, 540
—, toxicity of, 549
—, utilization of, 540, 541
Ethylene glycol ethers, in emulsifying agents, 543, 558
—, in mineral oil, 543
—, in penetrating agents, 558
—, in plasticizers, 558
—, in wetting agents, 558
—, preparation of, 500, 505, 543, 544, 557
—, solvent properties of, 543
Ethylene glycol ethyl ether, dewaxing agent for lubricants, 507
—, in brake fluid mixtures, 542
—, in candle wax, 543
—, in mineral oil, 538
—, solvent properties of, 543
—, toxicity of, 543
—, wetting properties of, 542
Ethylene glycol ethyl ether acetate, in refrigerants, 543
Ethylene glycol formal, solvent properties of, 542, 543
Ethylene glycol hypochlorite, reaction with olefins, 628
Ethylene glycol isobutyrate, plasticizer for cellulose acetate, 540
Ethylene glycol methyl ether, plasticizer from, 542
Ethylene glycol molybdate, from ethylene, 628
Ethylene glycol nitrate nitrite, from ethylene, 622
Ethylene glycol stearate, in shaving preparations, 540
Ethylene glycol trichloroacetate, *see* Trichloroacetyl glycol
Ethylene halohydrins, reaction with sodium carbonate, 533
Ethyleneimine, preparation of, 568
Ethylene oxide, catalyst, pyrolysis of butanes, 61
—, —, — propane, 61
—, —, decomposition of acetaldehyde, 884
—, dehydration agent for alcohols, 558
—, dioxane from, 579
—, emulsifying agents from, 566
—, esterification of, 540
—, estimation of, 556, 557
—, ethylene chlorohydrin from, 516
—, extraction agent for nicotine, 566
—, from *β*-chloroethyl acetate, 550
—, from dichlorodiethyl ether, 551
—, from ethylene, 552, 893
—, from ethylene chlorohydrin, 550
—, from ethylene glycol, 537
—, from ethyl hypochlorite, 551
—, from monochlorodimethyl ether, 551
—, from vinyl acetate, 553
—, hydration of, 557
—, in fuels, 566
—, in fumigants, 566
—, in insecticides, 565, 566, 569
—, in preparation of metallic oxide gels, 560
—, — sols, 560
—, in stabilization of aliphatic nitrates, 566
—, polyalkene glycol ethers from, 568
—, polymerization of, 562
—, properties of, 553, 554
—, pyrolysis of, 554, 555
—, reaction with aliphatic secondary amines, 561
—, — aluminum hydroxide, 560
—, — 2-aminoacetaldehyde, 561
—, — 2-aminopyridine, 561
—, — ammonia, 567
—, — aromatics, 563
—, — casein, 561
—, — cellulose, 558, 559
—, — cetylamine, 588
—, — dibenzylamine, 560
—, — dibutylnaphthalenesulphonamide, 562
—, — diethylene glycol, 558
—, — *β*-*γ*-dihydroxypropylaniline, 561, 570
—, — ethylene glycol, 544
—, — ethyl sodioacetoacetate, 565
—, — Grignard reagents, 564, 565
—, — horn, 561
—, — hydrogen chloride, 516, 560
—, — hydrogen sulphide, 463, 563, 564
—, — *β*-hydroxy-*γ*-alkoxypropylaminobenzene, 570
—, — isopropyl alcohol, 557
—, — lignin, 559
—, — mercaptans, 472, 564
—, — metal chlorides, 560
—, — oleyl alcohol, 558
—, — paraffins, 1101
—, — *m*-phenylenediamine, 560
—, — phenyl sodium, 563
—, — potassium thiocyanate, 564
—, — sodium bisulphite, 565
—, — stearic acid, 588
—, — thiourea, 564
—, — trichloroacetic acid, 540
—, — wool, 561
—, toxicity of, 556
Ethylene oxide derivatives, inhibitors, decomposition of chloroprene polymers, 682
Ethylene oxide polymers, structure of, 562
Ethylene polysulphide, preparation of, 499
Ethyl ether, as dielectric, 728
—, effect on sulphation of ethylene, 322
—, ethyl alcohol from, 421
—, from diethyl sulphate, 326
—, from ethylene, 322, 323
—, hydration of, 421
—, precipitant for asphaltenes, 1192
—, *see also* Diethyl ether
Ethyl fluoride, preparation of, 748
N-Ethylglycocoll, removal of hydrogen sulphide by, 458

Ethylhexaldehyde, reaction with acetone, 443
Ethylhydrindene, pyrolysis of, 94
Ethyl hydrogen sulphate, preparation of, 299
Ethyl hypochlorite, ethylene oxide from, 551
—, from ethyl alcohol, 346, 626
—, reaction with 1,4-dihydronaphthalene, 626
—, — hex-3-enoic acid, 627
Ethylidene chloride, preparation of, 716
Ethylidene compounds, preparation of, 315
Ethylidene diacetate, preparation of, 717
—, pyrolysis of, 718
Ethylidene radical, from ethane, 55
Ethyl iodide, reaction with ammonium sulphite, 819
—, — sodium plumbite, 829
—, — sodium sulphite, 819
Ethyl isovalerate, dewaxing agent, 353
Ethyl lactate, extraction agent, 44
Ethyl magnesium bromide, reaction with propene oxide, 586
—, — vinylacetylene, 708
Ethyl mercaptan, diethyl pentasulphide from, 481
—, effect on color stability, 454
—, — ethylene polymerization, 636
—, from acetylene, 720
—, from ethyl chloride, 822
—, in petroleum, 454, 1104
—, reaction with ethylene oxide, 472
Ethyl-α-methylcrotonic acid, preparation of, 451
Ethyl nitrate, catalyst, oxidation of benzene, 944
Ethyl nitrite, pyrolysis of, 1096, 1097
—, reaction with 1 (2′-phenyl) ethylcyclohexene-1, 619
Ethylnitrolic acid, from nitroethane, 1093
—, reduction of, 1094
Ethyl orthosilicate, catalyst, hydrogenation of sulphur compounds, 1248, 1249
3-Ethyl-2-pentene, reaction with aniline, 615
—, — ozone, 901
Ethyl peroxide-gasoline blends, as motor fuels, 1038, 1039
Ethylphenol, extraction agent for phenol, 391
o-Ethylphenol, from ethyl alcohol, 173, 347
Ethylplumbonic acid, preparation of, 829
Ethylpropiolic acid, preparation of, 511
Ethyl propionate, dewaxing agent, 353
—, from ethyl alcohol, 339
Ethyl radical, formation of, 50
Ethyl selenide, inhibitor, polymerization of chlorophene, 681
Ethyl sodioacetoacetate, reaction with ethylene oxide, 565
Ethylsorbitol ether, preparation of, 826
Ethyl sulphide, reaction with sodium hydrosulphide, 822
Ethylsulphuric acid, catalyst, ethylene-sulphuric acid reaction, 322
—, ethyl alcohol from, 326, 327
—, from ethyl alcohol, 343
—, from ethylene, 298, 321, 322
—, hydrolysis of, 319, 325, 326
—, reaction with ethyl alcohol, 332
—, — ethylene, 298
Ethyl thioacetate, preparation of, 438, 439
Ethyltoluene, from pinene, 88
—, from sapropelite tar, 144
—, from trimethylcycloheptane, 94
—, indene from, 156
—, in petroleum, 35
3-Ethyl-2,2,4-trimethyl-3-pentanol, reaction with iodine, 411
Ethyl xanthate, from ethyl alcohol, 355
Ethynylcyclohexanol, reaction with ozone, 904
Ethynylfenchyl alcohol, reaction with ozone, 904
Eugenol, inhibitor, polymerization of methyl vinyl ketone, 705
—, reaction with selenious acid, 446
Eutectics, as heat-transfer media, 861
Exanol, definition of, 675
Explosives, preparation of, 544, 622
"Extensive" property, definition of, 1272
Extraction agents, acetone as, 1070, 1071, 1105
—, aniline as, 30
—, butane as, 972
Extraction agents, calcium hydroxide as, 1107
—, calcium oxide as, 1105
—, chloroform as, 728, 1245
—, chlorohydrocarbons as, 972
—, dichloroethylene as, 1245
—, diethyl ether as, 1070, 1245
—, ethyl alcohol as, 1070, 1071
—, gasoline as, 975, 976, 1105 1155
—, green-acid soap as, 1071, 1072
—, hydrogen fluoride as, 1108, 1109
—, isopropyl alcohol as, 975, 1070, 1071
—, ketones as, 972
—, methyl alcohol as, 975, 977
—, naphthenic acids as, 1073
—, propane as, 972, 1071
—, pyridine as, 977
—, soda-lime as, 1106, 1107
—, sodium carbonate as, 1105, 1107
—, sodium chloride as, 1108
—, sodium hydroxide as, 1105-1107
—, sodium oxide as, 1105
—, sulphur dioxide as, 30, 1070, 1107
—, sulphuric acid as, 30
—, xylene as, 1107

F

Factice, preparation of, 468
Fat-denaturant, preparation of, 1080
Fats, autoxidation of, 914
—, from wax acids, 970
—, hydrolysis of, 1069
Fatty acids, by oxidation of paraffins, 865, 1088
—, degradation of, 19
—, foam-preventing agents from, 1080
—, from crude oil, 10
—, from hydrocarbon oils, 20
—, from petroleum, 17
—, in asphalt compositions, 1214
—, nitration of, 1088
—, oxidation of, rate, 931
—, petroleum from, 20
—, reaction with silicic-acetic anhydride, 1116
Fatty acid salts, as emulsifying agents, 1216
—, as insecticides, 1077
Fatty oils, action of bacteria on, 19
—, degradation of, 19
—, mineral oils from, 17
—, promoter, ethyl alcohol from ether, 333
Fehling's solution, reaction with asphaltogenic acids, 1195
Fenchone, as plasticizing agent, 681
Fenchyl alcohol, blending agent for motor fuel, 1035
Ferralloy, effect on pyrolysis of paraffins, 181
Ferric bromide, catalyst, esterification of propene, 316
Ferric chloride, catalyst, alkylation of phenols, 605
—, —, bromination of benzene, 791
—, —, chlorination of ethylene, 494
—, —, — methane, 726
—, —, — propane, 750
—, —, esterification of olefins, 301, 306, 307
—, —, fluorination of methane, 736
—, —, halogenation of cyclopropane, 761
—, —, in cracking, 132
—, —, polymerization of formaldehyde, 579
—, —, reaction of *m*-cresol and ammonia, 788
—, —, — dichloroethane and hydrogen fluoride, 747
—, —, — ether and hydrogen chloride, 345
—, —, — ethylene and hypochlorous acid, 515
—, —, — ethylene oxide and benzene, 563
—, —, — glycol ethers and formaldehyde, 582
—, —, — glycols and formaldehyde, 543
—, —, — phenol and butyl chloride, 818
—, —, — vinyl chloride and hydrogen chloride, 716
—, decolorizing agent for asphalt, 1192
—, effect on color stability, 927
—, in fireproofing agents, 1086
—, precipitant for nitro-asphaltenes, 1191
—, refining agent for gasoline, 263, 670, 929

Ferric compounds, catalysts, oxidation of hydrocarbons, 1043
Ferric compounds, *see also* Iron compounds
Ferric naphthenate, in paints, 1115
Ferric nitrate, desulphurizing agent, 490
Ferric oxide, antioxidant, paraffin oil oxidation, 907
—, catalyst, chlorination of benzene, 781
—, —, ethylation of amines, 346
—, —, hydration of acetylene, 714
—, —, hydration of vinylacetylene, 705
—, —, oleone from oleic acid, 446
—, —, oxidation of butyl alcohol, 880
—, —, — gasoline, 1058
—, —, — methane, 871
—, —, pyrolysis of methane, 218, 227
—, —, — natural gas, 190
—, —, reaction of acetylene and chlorine, 743
—, —, — carbon monoxide and steam, 276, 277
—, —, — methane and steam, 273
—, desulphurizing agent, 489
Ferric salts, reaction with *β*-sulphonic acids, 1065
Ferric sulphate, as refining agent, 928
—, catalyst, hydration of vinylacetylene, 705
—, desulphurizing agent, 490
Ferrous acetate, catalyst, oxidation of methyl ethyl ketone, 450
Ferrous chloride, as refining agent, 668
—, catalyst, *ter*-butyl chloride from isobutyl chloride, 752
—, —, chlorination of methane, 726
—, *see also* Iron compounds
Ferrous hydroxide, catalyst, hydrolysis of alkyl halides, 797, 801
Ferrous oxide, catalyst, cracking of wax acids, 979
Ferrous phosphate, catalyst, hydration of ethylene, 284
Ferrous sulphate, catalyst, bromination of benzene, 791
—, —, reaction of ethylene and hydrogen peroxide, 897
—, —, — ethylene and sulphuric acid, 323
—, reaction with hydroxymethylhydroperoxide, 887
Ferrous zinc sulphide, desulphurizing agent, 489
Filaments, action of triethanolamine on, 578
Films, wax acids in, 975
Fire brick, catalyst, polymerization of olefins, 1042
Fireclay, effect on production of carbon black, 240
—, — pyrolysis of methane, 227
Fire extinguishers, chlorofluoromethanes in, 738, 739
—, from carbon tetrachloride, 732, 733
Fireproofing agents, preparation of, 1086
First order reaction, definition of, 501
Flame gases, latent energy in, 1007
Flame propagation, effect on inflammability limits, 982, 983
—, in combustion, 1005, 1006
Flame temperatures, measurement of, 1007-1009
Flame velocities, of gases, 1009-1011
Flame velocity, effect of moisture on, 1010
Flash point, definition of, 1170
—, of benzine, 988
—, of ethyl alcohol, 988
—, of methyl alcohol, 988
—, of oils, determination of, 1170, 1171
Flooring compositions, asphalts in, 1213
Florida earth, adsorption of resins with, 1188
Floridin, as refining agent, 923
—, catalyst, depolymerization of triisobutylene, 645
—, —, polymerization of olefins, 642, 643, 649, 650
—, —, pyrolysis of olefins, 87, 88
Flotation agent, from disulphides, 486
—, from naphthalene, 488
—, from rosin, 466
Fluidity, of asphalt, effect of trisodium phosphate, 1219
Fluidity index, of asphalts, 1210
Fluorene, fluorenone from, 954, 955
—, oxidation of, 954, 955
—, reaction with ethyl magnesium bromide, 824
—, — propene, 594
Fluorenone, from fluorene, 954, 955
Fluorides, from aralkyl halides, 735
Fluorinated paraffin wax, in dielectrics, 759
Fluorination, of benzene, 791, 792
—, of cyclohexane, 773, 774
—, of *o*-dichlorobenzene, 792
—, of ethane, 747
—, of hexachlorobenzene, 792
—, of methane, 735, 736
—, of paraffin wax, 759
Fluorine, from potassium bifluoride, 759
Fluorine derivatives, of iodoform, properties, 737
Fluorobenzoic acid, from *p*-fluorotoluene, 954
Fluorochlorobenzenes, from *o*-dichlorobenzene, 792
Fluorochloro derivatives, from hexachlorobenzene, 792
Fluorochloromethanes, reaction with amines, 737
—, removal of acids from, 737
Fluorocyclohexane, preparation of, 773, 774
—, reaction with bromine, 774
—, stability of, 774
Fluorodichloroethane, from trichloroethane, 747
Fluorodichloromethane, as refrigerant, 547
—, from chloroform, 737
Fluoroform, from iodoform, 737
—, oxidation of, 737
p-Fluorotoluene, oxidation of, 954
Fluorotrichloromethane, carbon tetrachloride from, 737
—, dichlorodifluoromethane from, 737
9-Fluorylmagnesium bromide, preparation of, 824
Foam-preventing agents, from fatty acids, 1080
—, from mahogany sulphonates, 1080
Foots oil, oxidation of, 972
Forinaceous materials, as emulsifying agents, 1218
Formaldehyde, acetic acid from, 889
—, as emulsifying agent, 891
—, as precipitant for proteins, 890, 891
—, as refining agent for petroleum, 625
—, as stabilizing agent for bitumens, 891
—, azeotropic mixtures with water, 884, 885
—, benzyl alcohol from, 958
—, by hydrolysis of methyl chloride, 727
—, — methylene chloride, 728
—, by oxidation of acetylene, 902
—, — cracking gas, 881
—, — ethane, 856, 857, 872
—, — ethyl alcohol, 337, 879
—, — ethylene, 553
—, — kerosene, 860, 946
—, — methane, 264, 857, 858, 866, 867, 870, 880-883
—, — methyl alcohol, 877-879
—, — natural gas, 23, 862
—, — olefins, 893
—, — propane, 862, 863, 873
—, — propene, 553
—, chloral from, 731
—, chlorination of, 887
—, condensation of, 889
—, condensation with amines and phenols, 891
—, decomposition of, 883, 884
—, *p*-dioxane from, 579
—, effect on ethylene oxidation, 896
—, formyl chloride from, 887
—, from ethyl alcohol, 337
—, from hydroxymethylhydroperoxide, 887
—, hydroxymethylhydroperoxide from, 887
—, in synthetic plastics, 890
—, paraformaldehyde from, 877
—, polymerization of, 877, 887
—, reaction with alcohols, 889
—, — carbon tetrachloride, 731
—, — cracked distillates, 625
—, — dipentene, 624
—, — glycols, 543
—, — hydrogen peroxide, 887
—, — hydrogen sulphide, 463
—, — methyl chloride, 727
—, — methylene chloride, 728
—, — 2-methylpyridine, 623
—, — methyltetrahydropicoline, 623
—, — olefins, 624, 625

Formaldehyde, reaction with terpenes, 624
—, — thiocresol, 473, 474
—, recovery of, 884, 885
Formals, from aldehydes and alcohols, 889
Formic acid, by cracking sapropelite tar, 145
—, by oxidation of acetophenone, 450
—, — acetylene, 902, 904, 954
—, — butane, 859
—, — cracking gas, 881
—, — ethane, 856-858, 872
—, — ethylene, 553, 897
—, — kerosene, 860, 946
—, — mesitylene, 954
—, — methane, 857, 858, 883
—, — methyl isopropyl ketone, 450
—, — olefins, 893
—, — paraffin wax, 971
—, — phenylacetylene, 904
—, — propane, 858, 859
—, — propene, 553
—, catalyst, dehydration of alcohols, 410
—, —, hydration of olefins, 410
—, formyl fluoride from, 887
—, from carbon monoxide and hydrogen, 1244
—, from carbon monoxide and steam, 871
—, from hydroxymethylhydroperoxide, 887
—, in pickling inhibitors, 1041
—, reaction with cyclohexanol, 406
—, — diolefins, 698
—, — pentenes, 312
—, — potassium fluoride, 887
Formyl chloride, decomposition of, 887
—, from formaldehyde, 887
Formyl fluoride, from formic acid, 887
Forward process, of cracking, 123
Fractional distillation, of crude oil, 21
—, of gaseous hydrocarbons, 1138, 1139
Fractional extraction, of lubricating oils, 41
—, of vaseline, 40
Fractionation, of gasoline, 30, 31
Frankonite, catalyst, hydrolysis of chlorobenzene, 782
Free energy, application, in petroleum industry, 1295-1305
—, concept of, 1271, 1272
—, relation to entropy, 1275
—, — heat content, 1274, 1275
—, — work content, 1273
Free energy change, 1-butene from *n*-butane, 1284
—, cracking of *n*-tetradecane, 1297
—, dehydrogenation of paraffins, 1284, 1298
—, effect of catalysts, 1296
—, — pressure, 1296
—, — structure, 1286, 1288
—, — temperature, 1293-1295
—, evaluation of, 1276-1278
—, hydration of ethylene, 283, 284, 290, 1302, 1303
—, —, effect of temperature on, 1302, 1303
—, hydration of 1-hexene, 1303
—, — isobutene, 296, 1303
—, hydrogenation of benzene, 1298, 1299
—, — diisobutylene, 1300
—, — hexene, 1299
—, isomerization of *n*-butane, 1282
—, — cyclohexane, 1301, 1302
—, polymerization of 1-hexene, 1299, 1300
—, — isobutene, 641, 1300
—, reaction of isobutane and isobutene, 1301
—, reduction of carbon monoxide, 1303-1305
—, relation to equilibrium constant, 50, 1275, 1276
—, — heat of reaction, 50
—, — temperature, 99, 1275
—, significance of 1275, 1276
Free energy of formation, definition of, 1278
—, of acetaldehyde, effect of temperature, 1304
—, of acetylene, 1282-1284
—, —, effect of temperature, 1294
—, of alcohols, effect of temperature, 1294, 1295
—, of aromatics, 1284-1286
—, of benzene, 1225, 1226
—, —, effect of temperature, 1295
—, of carbon monoxide, effect of temperature, 1304
Free energy of formation, of naphthenes, 1225, 1226, 1284-1286
—, —, effect of temperature, 1294, 1295
—, of olefins, 1225, 1226, 1282-1285, 1295
—, —, effect of temperature, 1294, 1295
—, of paraffins, 1225, 1226, 1278, 1279, 1281, 1282, 1294, 1295
—, —, effect of temperature on, 1294, 1295
—, of water, 1275
—, —, effect of temperature on, 1304
Free energy relations, of oxygenated aliphatics, 1286
Free radicals, hydrocarbons from, 53
—, identification of, 50
—, in alkylation of hydrocarbons, 200
—, in pyrolysis of hydrocarbons, 50-52, 70, 71, 81
Freon, definition of, 737
Frothing agents, preparation of, 394, 417
Fuel oil, aquolysis of, 132
Fuels, by cracking methane, 1017
—, by oxidation of oils, 1047
—, combustion, mechanism of, 1012, 1013
—, isopropyl ether in, 1017
—, isopentane in, 1017
Fugacity, definition of, 1296
—, relation to pressure, 1322, 1323
Fuller's earth, adsorption agent, 1109
—, catalyst, reforming of gasoline, 189
—, —, hydrolysis of chlorobenzene, 782
—, —, ozonization of gasoline, 1045
—, —, polymerization of diolefins, 667
—, —, — isobutene, 642
—, —, pyrolysis of gaseous hydrocarbons, 223
—, desulphurizing agent, 1044
—, promoter, reduction of carbon monoxide, 1228
—, refining agent for gasoline, 928
—, sweetening agent, 479
Fumarex, definition of, 235
Fumaric acid, *dl*-tartaric acid from, 547
Fumigants, estimation of ethylene oxide in, 556
Fungicides, lead tetraalkyls in, 823
—, mercaptans in, 487
—, naphthenic acids in, 1112, 1113
—, phenols in, 818, 1112, 1113
—, sulphonates in, 1078
—, sulphur in, 1078
Furfural, extraction agent for olefins, 163
—, in brake fluid mixtures, 539
—, oxidation of, 945
—, reaction with cracked gasoline, 625
—, refining agent, 43, 930, 1202, 1205
—, *meso*-tartaric acid from, 945
Furfuraldehyde, *see* Furfural
Furfuraldoxime, extraction agent, 44
Furfuran, reaction with divinyl ether, 612
—, — hydrogen sulphide, 463
Furfurans, as extraction agents, 44
Furfurol, *see* Furfural
Furfuryl alcohol, extraction agent, 44
Furoperacid, estimation, of olefins, 1152
—, preparation of, 1152
Furoyl peroxide, catalyst, hydrogenation of olefins, 900

G

Gallium chloride, catalyst, benzene-benzoyl chloride reaction, 815
—, —, benzene-propyl chloride reaction, 815
Gardinol WA, definition of, 1084
Gas, effect of temperature on formation, 143
—, from gas oil, 102
—, from topped crudes, 140
Gas analysis, apparatus for, 1138, 1139
—, by density determination, 1134, 1135
—, by vapor pressure-temperature curves, 1136, 1137, 1138
—, general methods for, 1121
Gas black, preparation of, 235
Gases, from cracking, 140
Gasification, of coal, 1246
Gas oil, aquolysis of, 132
—, as demulsifying agent, 1107
—, coke from, 110

Gas oil, cracking of, 102, 111, 139, 140
—, from crude oil, 28
—, gasoline from, 143, 1045
—, heat content of, 1327, 1328
—, in insecticides, 978
—, motor fuel from, 1046
—, naphthenic acids in, 1103
—, nitration of, 1098, 1099
—, oxidation of, 863, 864
—, pyrolysis of, 178
—, reaction with steam, 273
—, sulphonic acids from, 1069
Gasol, alcohols from, 1255
—, aromatics from, 1255
—, definition of, 1242
—, from carbon monoxide and hydrogen, 1250
—, illuminating gas from, 1255
Gasoline, acids in, 908
—, action of aluminum chloride on, 212
—, aldehydes in, 908
—, alkylation, 593
—, analysis of, 28, 30, 195
—, anesthetic effect of, 1256
—, antioxidants for, 912, 914-919, 927
—, apparatus for detection of, 1132
—, aromatics in, 28, 32, 34, 136, 144, 196
—, aromatization of, 74, 179
—, as extraction agent, 976, 1105, 1155
—, as solvent, 46
—, autoxidation of, 907
—, azeotropes in, 30
—, by aquolysis, 132, 133
—, by oxidation of gas oil, 1045
—, chlorination of, 755
—, color stabilizers for, 926, 927
—, cracked, refining of, 216, 666-668, 909
—, cracking of, 109, 136, 139, 142, 154, 178, 179
—, cumarone in, 144
—, cycloparaffins in, 28, 31-34, 144
—, cyclopentadiene in, 144
—, distillation of, 30, 1169
—, effect of air on antiknock value, 1046
—, — light on, 924
—, — oxygen on, 924
—, — ozone on, 1044, 1045
—, — sulphur on, 924
—, estimation in gases, 1135, 1136
—, flame temperatures of, 1008 1009
—, formation of peracids in, 909
—, from acetylene, 704
—, from carbon monoxide and hydrogen, 1229, 1231, 1235, 1243, 1247, 1250-1252
—, from ceresin, 195
—, from coal tars, 135
—, from cracking petroleum distillates, 102, 140, 143, 195
—, from crude oil, 7, 28, 97
—, from Kogasin, octane number of, 1251
—, from natural gas, 21, 191
—, from olefins, 203, 209, 638-641, 646, 647
—, from sapropelite tar, 135, 144
—, from sludge oil, 134
—, from still vapors, 1047
—, gum formation in, 908-915, 917-919, 921, 924
—, heating value of, 142
—, hydrogenated, in varnish removers, 433
—, hydrogenation, to increase induction period, 909
—, ignition temperature of, 990, 991, 995, 996, 998
—, in alcohol distillation, 328
—, inflammability limits of, 985, 986
—, isoprene in, 144
—, lubricating oil from, 212
—, methods of adding antioxidants to, 914
—, natural, octane number of, 1033
—, olefins in, 136, 144, 155
—, oxidation of, 266, 267, 855, 861, 864, 908, 1046
—, oxidized, preparation of, 1046
—, oxidized, properties of, 1047
—, parachor, determination of, 1181
—, paraffins in, 24, 28, 32, 144
—, peroxides in, 908
—, piperylene in, 144
—, Raman spectra, determination of, 1183
Gasoline, reaction with antimony pentachloride, 1243
—, refining agents for, 134, 135, 490, 919, 927-930
—, reforming of, 112, 113, 116
—, sodium plumbite sweetening, 926
—, stabilization of, 24, 1112
—, tests for color stability, 925
—, vapor pressure, determination of, 1169
—, vapor-recovery, octane number of, 1033
—, *see also* Motor fuel
Gasoline-acetone blends, as motor fuels, 1038, 1039
Gasoline-air mixture, effect on octane number, 1030
Gasoline-alcohol-benzol blends, as motor fuels, 1038
Gasoline-alcohol blends, as motor fuel, 1034-1038
—, blending agents for, 1035
—, octane number of, 1251
Gasoline-benzol blends, as motor fuels, 1038
—, blending agents for, 1039
—, octane number of, 1251
Gasoline-ethyl ether blends, as motor fuels, 1038
Gasoline-ethyl peroxide blends, as motor fuels, 1038, 1039
Gasoline-isopropyl ether blends, as motor fuels, 1039
Gelatinizing agents, wax acids in, 975
Gels, metallic oxides, preparation of, 560
Generator gas, carbon monoxide from, 1246
—, hydrogen from, 1246
Geraniol, as blending agent, 1035
Germicides, from alkylated phenols, 604, 818
Glass, effect on benzene chlorination, 779
—, inhibitor, pyrolysis of paraffins, 153
Glass wool, catalyst, esterification of olefins, 311
Glow discharge, action on acetylene, 263
—, — butadiene, 650
—, — ethane, 257
—, — methane, 257, 263
—, — oils, 262
—, in cracking methane, 54
Glucose, in dust fixatives, 1079
Glue, formaldehyde in, 890, 891
—, reaction with ethylene oxide, 561
Glutaric acid, from cyclopentane, 876
Gluten, emulsifying agent for asphalts, 1218
Glycerol, acrolein from, 878
—, converting gels to sols with, 560
—, dehydration agent, 538
—, evaporation retardant, 746
—, from allyl alcohol, 895
—, hydrogenation of, 547
—, in cleaning agents, 1112
—, in decolorizing agents, 958
—, in dust fixatives, 1079
—, in polymerization of acetylene, 704
—, in vulcanization of rubber, 1078
—, in wetting agents, 1112
—, monochlorohydrin from, 516
—, preparation of, 507, 547
—, propene glycol from, 547
—, reaction with naphthenic acids, 1112
—, — resins, 217
—, solvent for butadiene, 174
Glycerol benzyl ethers, preparation of, 543
Glycerol monochlorohydrin formal, as solvent, 542, 543
Glycerol trichlorohydrin, preparation of, 507
Glyceryl naphthenate, in insecticides, 1112, 1115
Glyceryl oleate, in insecticides, 1115
Glyceryl trinitrate, reduction of sensitivity to shock, 546
Glycol, extraction of fuels by, 925
—, for absorption of olefins, 163
—, from ethylene, 895
—, from trimethylethylene, 547
—, in refining of gasoline, 930
Glycol diacetate, from ethylene dichloride, 496
Glycol dialkyl ethers, preparation of, 544
Glycol diethers, uses of, 544
Glycol esters, glycols from, 532
—, as absorbents, 738
—, as solvents, 549
Glycol ether esters, as plasticizers, 544

Glycol ethers, applications of, 544, 548, 549, 738
—, preparation of, 548
—, stabilized by triethanolamine, 577
Glycol monosulphuric acid, catalyst, sulphation of ethylene, 323
Glycols, dioxane, from, 578
—, from chlorohydrins, 524
—, from cracked gasoline, 854
—, from ethylene oxide, 557
—, from olefins, 532, 547, 624
—, reaction with aldehydes, 543, 582
—, — ketones, 582
—, — naphthols, 543
Glyoxal, decomposition of, 897, 898
—, from acetylene, 902, 904
—, from olefins, 895, 897
Glyoxal sulphate, preparation of, 829
Gold, catalyst, acetylene-amine reaction, 719
—, —, hydration of ethylene, 291
—, —, oxidation of olefins, 552, 553, 586
—, —, polymerization of acetylene, 705
—, —, pyrolysis of acetals, 715
Gold halide, catalyst, fluorination of alkyl halides, 747
Gold salts, in hydration of acetylene, 712
Gold vanadate, catalyst, hydration of ethylene, 291
Graphite, analysis of, 782
—, catalyst, cyclization of paraffins, 189
—, —, dehydrogenation of acenaphthenes, 955
—, —, pyrolysis of acetylene, 89
—, —, — benzene, 192
—, —, — methane, 180
—, dispersing agents for, 576
—, in lubricants, 731, 1079, 1116
Graphite grease, analysis of, 789
Graphitic carbon, catalyst, pyrolysis of methane, 218
Gravity-index, 1176
Grease, calcium soap in, 1079
—, from spindle oil acid sludge, 1058
—, petrolatum in, 1079
—, sodium mahogany sulphonate in, 1079
Green acids, as demulsifying agents, 1075
—, extraction by β,β'-dichloroethyl ether, 530
—, in insecticides, 1077
—, solubility of, 1065
Green acid salts, as emulsifying agents, 1074
—, separation of, 1071
Green acid soaps, as extraction agents, 1071, 1072
Green oil, burning oil from, 242
—, definition of, 242
—, lampblack from, 242
Grignard reagents, alcohols from, 886
—, reaction with aldehydes, 886
—, — ethylene oxide, 564, 565
—, — vinylacetylene, 708
Grozny oil, naphthenes from, 137
Grozny paraffin, cracking of, 138, 195
—, oxidation of, 846
Guaiacol, antioxidant for gasoline, 916
—, polymerization inhibitor, 705
Guanidine, in fungicides, 569
—, reaction with amines, 587
Gum, estimation in gasoline, 910-912
—, — kerosene, 912
—, from cracked gasoline, 1054
—, oxygen content of, 911
Gum acacia, in asphalt emulsions, 1219
Gumbrin, as adsorption agent, 1109
Gum content, effect of cracking on, 107
Gum flux, naphthenic hydrocarbons as, 915
Gum formation, depletion of inhibitors, 913
—, during storage of fuel, 909
—, dyestuffs as inhibitors for, 913
—, effect of chromic acid on, 924
—, — peroxide formation on, 924
—, — ultraviolet light on, 922, 924
—, in gasoline, 908-915, 917-919, 921, 924
—, —, inhibitors for, 914, 915
—, mechanism of, 921
Gum mastic, stabilizing carbon tetrachloride, 730
Gypsum, as dehydrating agent, 329, 365
Gyro process, of cracking, 119

H

Haber's cracking rule, 101
Hafnium tetrachloride, catalyst, alkylation of aromatics, 596
Hall process, of commercial cracking, 119
β-Haloethylarsines, preparation of, 526
Halogen acids, reaction with diolefins, 699
Halogenated alcohols, preparation of, 522, 523, 524
—, uses of, 523
Halogenated ethers, from butadiene, 698
Halogenated hydrocarbons, as solvents, 727
—, from natural gas, 23
Halogenated olefins, in drying oils, 1115
—, nomenclature of, 491
—, reaction with naphthenic acid salts, 1115
Halogenated paraffins, voltolization of, 262
Halogenation, of asphaltenes, 1191
—, cyclobutane, 762, 763
—, cyclopentane, 763, 764, 765
—, cracking gas, 146
—, diolefins, 683, 699, 700
—, hydrogen sulphide, 464
—, methylcyclohexane, 775
—, naphthenes, 760
—, olefins, 1152
—, toluene, 953
Haveg resin, corrosion inhibitor, 517
Heart, effect of cyclopropane on, 1266
—, — epinephrine on, 1269
Heat capacity, definition of, 1273, 1306
—, entropy change from, 1278, 1279
—, relation to entropy, 1273, 1306
—, — heat content, 1306
Heat content, definition of, 1306
—, determination of, 1327, 1328, 1329-1332
—, effect of pressure on, 1329
—, of gas oil, 1327, 1328
—, of naphtha, 1331, 1332
—, relation to entropy, 1341-1343
—, — free energy, 1275
—, — heat capacity, 1306
—, — internal energy, 1273
—, *see also* Enthalpy
Heat content change, effect of temperature on, 1293
—, evaluation of, from heat of combustion, 1277
—, free energy change from, 1276, 1277
—, relation to free energy change, 1274, 1275
—, — internal energy change, 1274
—, — pressure-volume product change, 1274
Heat of combustion, heat content change from, 1277
—, of acetylene, 1282-1284
—, of aromatics, 1284-1286
—, of cyclohexene, 1284, 1285
—, of naphthenes, 1284-1286
—, of olefins, 1282-1284
—, of *n*-paraffins, 1279, 1280, 1281
Heat of reaction, in cracking operation, 103
—, in isomerization of *n*-butane to isobutane, 1282
—, thermodynamic relations, 50
Heat of vaporization, determination of, 1325, 1327
Heat-transfer media, materials employed as, 544, 860-862
Heckmann process, of commercial cracking, 130
Hectopentacontane, from carbon monoxide and hydrogen, 1226
Helium, effect on acetylene polymerization, 267
—, — decomposition of acetaldehyde, 884
—, —, — ethylene oxide, 554
—, — ignition temperature, 998
—, — inflammability limits, 984, 985
—, — knocking, 1011, 1012
—, estimation of, 22, 1125, 1126, 1147, 1148
—, in natural gas, 21, 22, 1121
Hemimellitine, from kerosene, 36
Heptadecaldehyde, condensation of, 889
Heptadecene, in kerosene, 145
Heptaldehyde, azeotropic mixture with isopropyl alcohol, 369
Heptane, alcohols from, 859, 865
—, dehydrogenation of, 99
—, explosive characteristics of, 1011
—, from di-*n*-heptyl mercury, 71

Heptane, from petroleum, 32, 144
—, 1-heptene from, free energy change, 1284
—, inflammability limits of, 980, 981, 985, 986
—, inflammation temperature of, 899
—, isomerization of, 71, 202
—, isomers, molal entropy, 1289
—, molal entropy of, 1288
—, oxidation of, 843, 850, 851, 859, 865, 873-875, 899, 1015, 1016
—, pyrolysis of, 71-73, 154
—, reaction with aluminum chloride, 198, 200
—, — molybdenum sulphide, 72
—, — nitric oxide, 1091
—, reference standard in knock rating, 1025, 1026, 1027
—, use in alcohol distillation, 329
—, — motor fuel, 1039
1-Heptene, blending octane number of, 1026, 1027
—, from *n*-heptane, free energy change, 1284
—, inflammation temperature of, 899
—, knock rating of, 1026, 1027
—, molal entropy, 1291
—, reaction with hydrogen bromide, 317
3-Heptene, inflammation temperature of, 899
—, oxidation of, 875
Heptenes, effect of tetraethyl lead on, 1021
—, from carbon monoxide and hydrogen, 1243
—, in gasoline, 144
—, oxidation of, 898, 899
Hepten-3-en-2-one, reaction with acetyl chloride, 612
Heptyl alcohol, from petroleum ether, 853
—, reaction with acetic acid, 406
sec-Heptyl alcohol, from olefins, 404
—, solubility in water, 404
sec-Heptyl esters, use as plasticizers with cellulose nitrate, 409
1-Heptyne, preparation of, 722
—, reaction with ozone, 904
Heptynes, effect of tetraethyl lead on, 1021
Hexabromobenzene, from benzene, 790, 791
Hexabromocyclobutane preparation of, 763
Hexabromoethane, preparation of, 747
Hexachlorobenzene, in chlorinated coal, 730
—, fluorination of, 792
Hexachlorobutane, from butene dichloride, 510
Hexachlorobutene-2, from hexachlorobutane, 510
Hexachloroethane, from carbon tetrachloride, 731
—, from ethylene dichloride, 501
—, from perchloroethylene, 742
—, in chlorinated coal, 730
—, reaction with antimony trichloride, 748
Hexachloropropene, preparation of, 812
Hexachloropyrene, oxidation of, 956
6,10-Hexadecadiyne, reaction with ozone, 904
Hexadecane, antioxidant, paraffin oil oxidation, 907
—, autoxidation of, 907
—, reaction with aluminum chloride, 202
Hexadecane-1,2-diol, from hexadecene-1, 548
Hexadecene, from isobutene, 643
—, oxidation by hydrogen peroxide, 548
—, reaction with persulphuric acid, 309
Hexadecylphenyl acetylene, antioxidant, for gasoline, 918
Hexadeuteriobenzene, preparation of, 273, 725
Hexadiene, by pyrolysis of cyclohexane, 93
—, — ethyl alcohol, 173
—, co-polymerization with trimethylethylene, 216
1,5-Hexadiene, *see* Diallyl.
Hexaethylbenzene, from ethylene and cyclohexane, 601, 602
—, from gaseous olefins, 209
Hexaethylene glycol dichloride, reaction with diethylene glycol, sodium salt, 544, 545
Hexafluoroethane, diluent, fluorination of benzene, 792
Hexahydronaphthalene, as blending agent, 1035
Hexamethylbenzene, molal entropy, 1289, 1290
Hexamethylene derivatives, in gasoline, 33
Hexamethylenetetramine, as adsorbent, 885
—, benzoylation of, 888
—, from methane, 264, 882
—, in pickling solution, 890
—, in preparation of resins, 1058
—, in stabilizing carbon tetrachloride, 730, 731
Hexamethylenetetramine, reaction with acetic anhydride, 888
—, structure of, 887, 888
Hexamethylethane, from pentamethylethyl bromide, 759
Hexane, action of silent discharge on, 257
—, aldehydes from, 1014
—, auto-ignition of, 1017
—, combustion of, 1005, 1014
—, cracking of, 111
—, dehydrogenation of, to benzene, 73
—, effect on photochemical decomposition of acetone, 450
—, effect on reaction of hydrogen bromide and allyl acetic acid, 318
—, — and pentene, 317
—, — and propene, 306, 307
—, entraining agent, alcohol distillation, 327
—, explosive characteristics of, 1011
—, flocculating agent for asphalts, 1196
—, free energy of formation, 1225, 1226, 1295
—, from carbon monoxide and hydrogen, 1243
—, from hexene, 1299
—, from petroleum, 32, 144
—, hydrogen from, 273
—, ignition temperature of, 992
—, inflammability limits of, 980, 981, 985, 986
—, isomerization of, 70, 198-201
—, oxidation of, 850 851, 1014
—, peroxides from, 1014
—, photochemical decomposition of, 267
—, pyrolysis of, 69-71, 153
—, reaction with acetyl chloride, 445
—, — aluminum chloride, 198-201
—, — benzene, 602, 603
—, — chlorine, 756
—, — nitric oxide, 1091
—, — nitrogen tetroxide, 1090
—, — nitrosyl chloride, 1101
—, — steam, 273
—, solvent, decolorizing resins, 216
—, —, for ketene, 435
—, —, separation of acetylene from gas mixtures, 169
Hexanol, from butyl alcohol, 339, 340
—, from ethyl alcohol, 339-341, 347
—, from hexene, 313
—, from hexenol, 173
—, from petroleum ether, 853
sec-Hexanol, from 1-hexene, free energy change, 1303
—, from olefins, 404
—, solubility in water, 404
—, solvent in ozocerite refining, 409
2-Hexanol, preparation of, 388
3-Hexanol, preparation of, 388, 389
2-Hexanone, from 2-nitrohexane, 1094
Hexanitrodiphenylamine, as antiknock, 1017
Hexatriacontane, reaction with aluminum chloride, 201, 202
Hexene, detonating properties of, 1017
—, dodecene from, 1299, 1300
—, free energy of formation, 1225, 1226, 1295
—, from ethyl alcohol, 173
—, from ethylene, 258
—, from hexane, 257
—, from *n*-nonane, 72
—, from propene, 75
—, from *n*-tetradecane, 1297
—, hexane from, 1299
—, hydration of, free energy change, 1303
—, hydrogenation of, free energy change, 1299
—, isomerization of, 87, 643
—, polymerization of, free energy change, 1299, 1300
—, reaction with benzene, 591, 598
Hexenes, from carbon monoxide and hydrogen, 1243
—, from propene, 75, 79, 639, 641
—, hexanols from, 388
—, in gasoline, 144
—, polymerization of, 643
—, reaction with formic acid, 312
—, — sulphuric acid, 308, 388, 389

Hexene-1,2-oxide, preparation of, 589
Hexene-1,2-oxide, reaction with hydrobromic acid, 589
Hex-3-enoic acid, reaction with ethyl hypochlorite, 627
Hexone, *see* Methyl isobutyl ketone
Hexylacetylene, preparation of, 722
Hexyl alcohol, *see* Hexanol
2-Hexylamine, from 2-nitrohexane, 1094
Hexyl chloride, formation of, 306
sec-Hexyl esters, plasticizers, cellulose nitrate, 409
sec-Hexyl mercaptan, in petroleum, 454
ter-Hexyl formate, preparation, 312
Hexylresorcinol, stabilizing agent, 328
1-Hexyne, preparation of, 146, 722
—, reaction with ozone, 904
Hillman test, for color stability of kerosene, 925
Horn, reaction with ethylene oxide, 561
Houdry process, of commercial cracking, 125-129
Humic acids, as emulsifying agents, 1099, 1218
Hydration, of acetylene, 712, 713, 714
—, butenes, 293-296
—, divinylacetylene, 709
—, ethylene, 282-291
—, —, free energy change, 1302, 1303
—, 1-hexene, free energy change, 1303
—, isobutene, 294-296
—, —, free energy change, 1303
—, 2-methylbutene-2, 296, 297
—, 2-methylpropene, 296, 297
—, propene, 288, 291, 292, 293
—, vinylacetylene, 705
Hydraulic cement, alkylolamine soaps in, 575
Hydrazine, as antiknock, 1018
—, reaction with aldehydes, 886
—, — ketones, 448
Hydrazobenzene, antioxidant, for gasoline, 917
Hydriodic acid, catalyst, isomerization of cyclohexane, 1302
Hydroabietic acid esters, emulsifying agents for asphalts, 1217
Hydroaromatics, *see* Cycloparaffins
Hydrobiphenyl, from benzene, 95
Hydrobromic acid, effect on hydration of olefins, 410
—, reaction with butadiene, 699
—, — hexene-1,2-oxide, 589
Hydrocarbons, pressure-volume-temperature relations, 1320, 1321
—, reaction with steam, 277, 278, 280
—, — sulphur, 467, 468
Hydrocarbon number, effect, on knock rating, 1027, 1028
Hydrocarbon oils, extraction with sulphur dioxide, 212, 1070
—, oxidation of, 1045, 1061
Hydrocarbon structure, effect, on knock rating, 1024, 1025, 1027, 1028
—, — lead susceptibility, 1033
Hydrochloric acid, acidation with, 9
—, catalyst in condensation of acetone, 431
—, —, cracking, 114
—, —, dehydration of tertiary alcohols, 410
—, —, esterification of isopropyl alcohol, 377
—, —, ethyl alcohol from ether, 333
—, —, ethylene-carbon monoxide reaction, 893
—, —, hydration of olefins, 297, 410
—, for extraction of nitrogen bases, 833
—, from carbon tetrachloride, 731
—, in estimation of ethylene oxide, 556
—, — lead tetraethyl in gasoline, 1165
—, in purification of triethanolamine, 567
—, in refining gasoline, 669
—, reaction with ethylene glycol, 537
—, — monovinylacetylene, 680
—, — olefins, 310, 311
—, — *sec*-nitropropane, 1096
Hydrocyanic acid, from hydrocarbon gas, 851
—, from methane and ammonia, 871
Hydrofined naphthas, in sulphate detergents, 1086
Hydrofluoric acid, effect, on ignition temperatures, 986, 987
—, promoter, mercury catalysts, 717
Hydroformed naphthas, in sulphate detergents, 1086
—, oxidation of, 1054
Hydrogen, antioxidant, for gasoline, 918
—, as motor fuel, 1040
—, by pyrolysis of aromatics, 95, 96
—, — cycloparaffins, 90, 92, 93
—, — ethylene oxide, 554
—, — olefins, 74-76, 79, 81, 83, 85-87, 166
—, — paraffins, 52, 60-65, 68-72, 149-151, 154, 161, 165, 168, 180, 218-229, 234, 269, 1247
—, combustion of, 1003, 1004
—, —, for supplying heat in pyrolysis reactions, 168
—, deasphalting agent, 45
—, diluent, oxidation of ethylene, 552
—, —, pyrolysis of hydrocarbons, 167, 179, 220
—, effect on chlorination of olefins, 492, 493
—, — cracking, 138
—, — electrical decomposition of hydrocarbons, 254
—, — polymerization of acetylene, 703
—, —, — ethylene, 166, 639, 647
—, — pyrolysis of hydrocarbons, 37, 79, 89, 95, 219
—, — thermal decomposition of ethylene oxide, 554
—, — voltolization, 261, 262
—, estimation of, in gases, 1127, 1128
—, formation during cracking, 99, 108, 131, 137, 138, 140, 1297
—, for preparation of cracking catalysts, 112
—, for removal of sulphur compounds, 1248, 1249
—, from carbon dioxide and methane, 273, 274
—, from carbon monoxide and steam, 277
—, from coal, 1246
—, from coke-oven gas, 1246-1248
—, from ethyl alcohol, 339-341, 347, 348, 352
—, from generator gas, 1246
—, from hydrocarbons and steam, 220, 229, 269-280, 1247
—, —, by action of electric arc, 226, 253-255
—, —, by action of silent discharge, 257, 259, 260
—, —, by oxidation, 269, 1246
—, —, by photochemical decomposition, 267
—, from iron and steam, 269
—, from water, 256, 269
—, from water gas, 269, 1247
—, ignition of, 1001
—, ignition temperature of, 987, 988, 997
—, in estimation of olefins, 1145, 1146
—, in estimation, of sulphur, 1157
—, in natural gas, 17, 21
—, in oil cracking, 113, 115
—, in recovery of wax acids, 976
—, inflammability limits of, 982, 983, 985
—, oxidation with copper oxide, 165, 659, 660
—, purification of, 234
—, reaction with acetone, 432
—, — acetyl chloride and ethylene dichloride, 501
—, — acetylene, 171, 719
—, — aldehydes, 885, 889
—, — asphaltenes, 1192
—, — benzene, free energy change, 1298
—, — butadiene, 699
—, — butyl lactate, 546
—, — carbon, 168, 1278
—, — carbon dioxide, 661, 1241, 1242
—, reaction with carbon monoxide, 660, 661
—, —, effect of catalysts on, 1228-1230
—, —, mechanism, 1224, 1225
—, —, thermodynamics, 1225, 1227, 1303-1305
—, reaction with cyclopropane, 761
—, — diisobutylene, free energy change, 1300
—, — divinylacetylene, 709
—, — glycerol, 547
—, — hexene, free energy change, 1299
—, — maleic acid, 945
—, — mercaptans, 1248, 1249
—, — naphthalene, 1154
—, — nitromethane, 1094
—, — olefins, 57, 58, 1145, 1146, 1154, 1245
—, — peanut oil, 1154
—, — petroleum hydrocarbons, 18, 138

Hydrogen, reaction with phthalic anhydride and carbon dioxide, 950
—, — sulphur, 1157
—, — sulphur compounds, 1248, 1249
—, — thiophene, 484, 485
—, — toluene, 347
—, — unsaturates, 1153, 1154
—, removal, by salt solutions, 457
—, —, from cracking gas, 657, 659, 660, 661
—, —, from gas mixtures, 1133
—, —, from olefins, 165
—, to improve carbon black, 248, 249
Hydrogenated cyclic compounds, 688
Hydrogenated oils, as lubricants, 576
—, autoxidation inhibitors for, 914
Hydrogenated safety fuel, ignition of, 1002
Hydrogenated tar, voltolization of, 262
Hydrogen bromide, catalyst, bromination of ethylene, 503
—, —, halogenation of cyclopropane, 761
—, reaction with allyl acetic acid, 318
—, — butadiene, 686
—, — methylacetylene, 723
—, — olefins, 298, 307, 315-318
—, — styrene, 318
—, — vinyl halides, 315, 716
Hydrogen chloride, catalyst, chlorination of cyclohexane, 766
—, —, — ethylene dichloride, 501, 742
—, —, condensation of polyhydric alcohols, 579
—, —, hydration of ethylene, 288
—, —, isomerization of cyclohexane, 1302
—, —, polymerization of aldehydes, 579
—, —, — olefins, 665
—, —, pyrolysis of hydrocarbons, 158, 168
—, —, reaction of aldehydes and cracked distillates, 625
—, —, — glycols and formaldehyde, 543
—, —, — hydrocarbons and aluminum chloride, 199-201, 203, 204, 207, 215
—, —, — olefins and carbon monoxide, 446, 625
—, —, — polyglycols and arsenious oxide, 545
—, diluent, chlorination of methane, 726
—, effect, on ignition temperature of hydrogen, 998
—, electrolysis of, 780
—, estimation of, in gases, 1127
—, in preparation of aluminum chloride catalyst, 196, 204, 214
—, reaction with acetone, 429
—, — acetylene, 716
—, — benzene, 950
—, — diethyl sulphate, 327
—, — diolefins, 686
—, — ether, 345
—, — ethyl alcohol, 345, 742
—, — ethylene glycol, 537
—, — ethylene oxide, 560
—, — gasoline, 928
—, — monovinylacetylene, 680, 706
—, — olefins, 204, 302, 303, 306, 310, 311
—, — 1-(2'-phenyl) ethylcyclohexene-1 and ethyl nitrite, 619
—, — vinyl esters, 716
— to remove iron from acetylene black, 244
Hydrogen chloride molybdic anhydride complex, reaction with ethylene, 628
Hydrogen content, characterization factor from, 1309
Hydrogen cyanide, from methane and ammonia, 280, 281
—, from nitric oxide and methane, 281
—, reaction with aldehydes, 886
—, — ketones, 448, 451
Hydrogen fluoride, diluent, fluorination of benzene, 792
—, extraction agent, 1108, 1109
—, fluorinating agent, 735
—, from fluoroform, 737
—, reaction with acetylene, 716
—, — carbon disulphide and chlorine, 737
—, — dichloroethane, 747
—, — olefins, 307
—, — unsaturated acids, 307
Hydrogen halides, catalysts, reaction of carbon monoxide and methanol, 1050
—, —, reaction of carbon monoxide and olefins, 625, 626
—, reaction with acetylene, 716
Hydrogen iodide catalyst, formation of biphenyl, 191
—, reaction with isopropyl hydroperoxide, 382
—, — propene, 316, 317
—, — vinyl chloride, 716
Hydrogen-nitrogen mixture, preparation of, 277
Hydrogen peroxide, effect on pentene-sulphuric acid reaction, 318
—, in estimation, of sulphur, 1125, 1161, 1162
—, reaction with acetone, 432
—, — aliphatic acids, 852
—, — cyclohexene, 852
—, — diisopropyl sulphate, 381
—, — ethylene, 897
—, — formaldehyde, 887
—, — hexadecene-1, 548
—, — lead mercaptides, 475
—, — olefins, 547, 895
—, — trimethylethylene, 547
—, refining agent, lignite spirits, 928
—, stability in tertiary butyl alcohol, 895
—, sweetening agent, 478, 490
Hydrogen polysulphide, reaction with divinylacetylene, 709
Hydrogen sulphide, action of electrical discharge on, 463
—, adsorption by charcoal, 461
—, catalyst, formation of *ter*-butyl acetate, 412
—, corrosion by, 456
—, detection of, 466, 1259
—, effect on carbon black yield, 237
—, — deposition of carbon, 192
—, — Kogasin synthesis, 1236
—, estimation of, 1125
—, from mercaptans, 478
—, ignition temperature of, 987
—, in natural gas, 22, 1121
—, in petroleum, 454
—, oxidation of, 460, 461
—, properties of, 461, 462
—, reaction with acetylene, 720
—, — di-*ter*-butyl sulphate, 463
—, — ethylene oxide, 463
—, — formaldehyde, 463
—, — furan, 463
—, — halogens, 464
—, — isoprene, 463
—, — olefins, 462, 463
—, — phosphoric acid, 466
—, — rosin, 466
—, recovery from spent alkali, 458
—, removal of, 23, 165, 170, 398, 457-460, 573-575, 1249
—, solubility, 461, 462
—, sulphuric acid from, 464
Hydrolysis, of *ter*-amyl acid sulphate, 394
—, *ter*-amyl bromide, 803
—, amyl chloride, 801-803
—, *sec*-amyl sulphate, 395
—, *ter*-butyl acid sulphate, 394
—, butyl halides, 797-800
—, carbyl sulphate, 1081
—, chlorobenzene, 782, 783, 784
—, chlorotoluene, 794
—, of cyanohydrins, 886
—, dibromocyclobutane, 762, 763
—, dibromocyclopropane, 762
—, *o*-dichlorobenzene, 785
—, 1,2-dichloro-2-methylpropane, 797
—, dihaloethanes, 532
—, disodium naphthalene, 958
—, ethyl chloride, 796, 797
—, ethylene chlorohydrin, 518, 519, 533
—, ethylene dichloride, 533, 797
—, ethylsulphuric acid, 319, 325, 326
—, fats, 1069
—, isobutyl bromide, 799
—, isobutyl chloride, 798
—, isopropyl chloride, 797

Hydrolysis, isopropyl hydrogen sulphate, 325
—, lead mercaptides, 471
—, methyl chloride, 727, 728, 796
—, methylene chloride, 728
—, polypropene sulphone, 618
—, sulphonic acids, 1067, 1068, 1081
—, 1,2,3-trichloro-3-methylpropane, 797, 798
Hydrolyzing agents, sulphonic acids as, 1069
Hydrophilic lipins, preparation of, 545
—, utilization of, 545, 546
Hydroquinone, as antioxidant, 337, 855, 907, 913, 914, 917
—, effect on color stability, 926
—, from benzene, 942
—, from benzoquinone, 953
—, inhibitor, ketone cyanohydrin polymerization, 451
—, promoter, oxidation of oils, 1044
—, quinone from, 1277
—, reaction with isopropyl hydroperoxide, 382
Hydroquinone dianilide, as antioxidant, 918
—, effect on color stability, 926
Hydroquinone phenyl ether, as heat-transfer medium, 861
Hydrorubber, motor fuel from, 1040
Hydrothiophenes, *see* Thiophanes
p-Hydroxyacetonitrile, as antioxidant, 915
Hydroxy acids, dehydration of, 968
—, effect on color stability, 937
—, from bromo acids, 447
—, from ceresins, 975
—, from lubricating oil, 855
—, from paraffin wax, 971
—, from petroleum, 963
—, reaction with ketene, 438
Hydroxyaldehyde, from ethylene glycol, 536
Hydroxyalkylamine esters, effect on color stability, 927
Hydroxyalkylamines, preparation of, 570
—, reaction with carbonic acid, 569
Hydroxyalkylcellulose, preparation of, 559
Hydroxyaryl ethers, as antioxidants, 938
Hydroxyazobenzene, as antioxidant, 917
Hydroxyazo compounds, condensation with cyclopentadiene, 692, 693
Hydroxybiphenyl, *see* Phenylphenol
Hydroxychrysenes, as antioxidants, 918
2-Hydroxycyclohexylcarbinol, from cyclohexene, 624
3-Hydroxy-3,4-di*ter*-butyl-1-butene, reaction with oxalic acid, 679
Hydroxyethylamine, from ethylene oxide, 560
β-Hydroxyethylarsenous acid, preparation of, 527
β-Hydroxyethylarsonic acid, preparation of, 527
Hydroxyethyl ethers, utilization of, 558
Hydroxyethyllignin, preparation of, 559
1-Hydroxyethyl-5-naphthol, preparation of, 569
1-*β*-Hydroxyethylpyridoneimine, preparation of, 561
β-Hydroxyethyl sulphonate, preparation of, 565
Hydroxyethyl thioethers, preparation of, 564
2-Hydroxy-3-isopropylbenzoic acid, formation of, 308
Hydroxyketo acids, preparation of, 843, 1053
Hydroxyketone, preparation of, 536
Hydroxylamine, from nitrolic acids, 1094
—, reaction with aldehydes, 886
—, — ketones, 448
Hydroxylamine esters, as wetting agents, 576
Hydroxylation, of olefins, 532, 534, 535, 547, 895, 897
—, of paraffins, 844-846
Hydroxymanganese acetate, catalyst, acids from alcohols, 1050
o-Hydroxymesitylenic acid, from mesitylene, 954
4-Hydroxy-4-methyl-2-hexanone, preparation of, 433
5-Hydroxy-5-methyl-3-hexanone, preparation of, 433
Hydroxymethylhydroperoxide, preparation of, 887
Hydroxyphenanthrenes, as antioxidants, 918
Hydroxyphenylazo-*α*-naphthol, as antioxidant, 916
Hydroxyphenylglycine, as antioxidant, 915
Hydroxypicenes, as antioxidants, 918
α-Hydroxypropionic acid, *see* Lactic acid
Hydroxypropylamines, preparation of, 585
Hydroxystearosulphuric acid, catalyst, sulphation of propene, 358
Hydroxysulphones, from butadiene sulphone, 695, 696
Hydroxytetrahydroquinoline, as antioxidants, 918
Hydroxy thioethers, reaction with thionyl chloride, 526
Hymolal, definition of, 1082
Hypochlorites, desulphurizing agents, 490
—, sweetening agents, 475, 478
Hypochlorous acid, desulphurizing agent, 115, 490
—, reaction with 2-butene, 509, 547, 548
Hypochlorous esters, reaction with olefinic acids, 627
Hypohalites, catalyst, oxidation of oils, 1054
Hypohalites, reaction with vinylacetylene, 706

I

Ichthyols, definition of, 1080
Icterus index, definition of, 1261
Igepons, detergent properties of, 1082, 1084
—, structure of, 1082, 1084
Ignition, by compression, 1000, 1001
—, by electrical discharge, 1001, 1002, 1009, 1010
—, by heated surfaces, 986, 987
—, effect on octane number, 1030
Ignition temperature, determination of, 987, 988
—, effect of antiknock compounds, 996
—, — catalysts, 1000, 1001
—, — concentration, 989-992
—, — hydrocarbon structure, 998, 999
—, — knock-inducing compounds, 996
—, — metal oxides, 1000
—, — pressure, 992-996
—, — water vapor, 996, 997
—, of acetylene, 988
—, ammonia, 987
—, benzene, 987, 988, 1000
—, butane, 992
—, carbon black, 245
—, carbon disulphide, 987
—, carbon monoxide, 987, 988, 997
—, cyanogen, 987
—, diethyl ether, 987-989
—, ethane, 987-989, 992, 993
—, ethylene, 987-989
—, gasoline, 990, 991, 995, 996, 998
—, hexane, 992
—, hydrogen, 987, 988, 997
—, hydrogen sulphide, 987
—, isobutane, 992
—, isooctane, 991, 992
—, methane, 986-988, 992, 993, 995-997
—, octane, 991
—, pentane, 987, 988, 992, 995, 1000
—, propane, 988, 989, 992, 993
—, propene, 988
Ignition-temperature depressants, nitro compounds as, 1097
Illuminating gas, from Gasol, 1255
—, from polymerization gases, 674
Imides, as antioxidants, 915
Impregnating agents, from halogenated wax, 759
Indanes, preparation of, 649
Indene, chlorohydrin from, 626
—, from cracking gas, 645, 646
—, from dicyclopentadiene, 156
—, from natural gas, 155, 183
—, from propene and benzene, 156, 645
—, from toluene and ethylene, 156, 645, 646
—, resins from, 155
Indoles, extractants for asphalts, 1202
Indophenol, as antioxidant, 913
Inflammability limits, definition of, 980
—, effect of flame propagation, 982, 983
—, — inert gases, 983-986
—, — pressure, 980
—, — temperature, 980-982
Infra-red rays, absorption by hydrocarbons, 32
Insecticides, acetaldehyde in, 891
—, alcohols in, 790, 1059, 1078
—, aluminum sulphate in, 1112
—, benzene in, 733
—, calcium caseinate in, 1112

Insecticides, carbon tetrachloride in, 732, 733
—, casein in, 1077
—, castor oil in, 1077
—, chlorobenzenes in, 782, 790
—, chloroethanes in, 745
—, derris in, 1078
—, disulphides in, 1112
—, efficiency of, 1058-1060
—, fatty acid soaps in, 1077
—, glyceryl oleate in, 1115
—, green acids in, 1077
—, Kontakt as, 1077
—, lead tetraalkyls in, 823
—, mahogany acids in, 1077
—, mercaptans in, 487, 1112
—, naphthenates in, 1112, 1114, 1115
—, naphthenic acids in, 487, 1112, 1113
—, β-naphthol in, 790
—, nicotine sulphate in, 1077, 1078
—, Penetrol in, 1078
—, petroleum distillates in, 545, 790, 978, 1058, 1059, 1077, 1078, 1112, 1115
—, phenols in, 487, 1112, 1113
—, polyglycol arsenites in, 545
—, pyrethrum in, 1078
—, rhodanates as, 1059
—, rosin in, 790
—, sulphonic acids as, 487, 1077, 1078
—, sulphonates in, 1077, 1078
—, sulphur in, 1114
—, sulphur dioxide in, 1077
—, wax acids in, 978
Insulating oil, carbon black in, 251
—, oxidation of, 930, 939
—, preparation of, 937
Intensive property, definition of, 1272
Internal energy, relation to heat content, 1273, 1274
Iodine, adsorption with carbon black, 249, 252
—, catalyst, aquolization, 132
—, —, bromination of benzene, 790, 791
—, —, — toluene, 795
—, —, condensation of ethylene glycol, 544
—, —, cracking, 114
—, —, dehydration of *ter*-alcohols, 411
—, —, fluorination of benzene, 792
—, —, hydroxylation of olefins, 535
—, —, pyrolysis of benzene, 95, 191
—, —, — propane, 158
—, inhibitor, polymerization of chloroprene, 681
—, reaction with acetone, 424, 430
—, — acetylene, 711
—, — cyclohexene, 629, 774, 775
—, — ethylene, 505, 629
—, — hydrogen sulphide, 1125
—, — lead tetraethyl, 1165
—, — methylene radicals, 51
—, — sodium acetylide, 711
—, — sulphur dioxide, 1125
—, — unsaturates, 491, 1125
Iodine chloride, catalyst, chlorination of ethylene, 495
—, —, chlorination of propene, 507
Iodine halides, reaction with unsaturates, 1152
Iodine number, of gasoline, 1045
Iodine pentoxide, reaction with carbon monoxide, 1128
Iodoalkyl nitrates, preparation of, 629
Iodobenzene, amines from, 787
—, reaction with potassium amide, 787
Iododifluoromethane, preparation of, 737
Iodoform, di-iodofluoromethane from, 737
—, fluoroform from, 737
—, from acetone, 430
—, iododifluoromethane from, 737
—, structure of, 729
2 Iodopentane, preparation of, 763
Iodosilver benzoate, reaction with acetylene, 711
—, — butadiene, 697
Iron, catalyst, acetone from acetaldehyde, 423
—, —, bromination of ethane, 747
—, —, — benzene, 790, 791
—, —, carbon from carbon monoxide, 229
—, —, chlorination of acetylene, 743
Iron, catalyst, chlorination of benzene, 778, 779
—, —, — carbon disulphide, 730
—, —, — difluoromethane, 734, 735
—, —, — ethane, 741
—, —, — olefins, 493
—, —, — toluene, 793
—, —, combustion of natural gas, 225
—, —, cracking, 112, 114
—, —, fluorination of benzene, 791
—, —, halogenation of dibromocyclobutane, 763
—, —, — of naphthenes, 760
—, —, — petroleum distillates, 490
—, —, hydration of ethylene, 291
—, —, oleone from oleic acid, 446
—, —, oxidation of ethylene, 552, 553, 893
—, —, — kerosene, 965
—, —, — lubricants, 932
—, —, — methane, 869
—, —, — naphthenes, 940
—, —, polymerization of acetylene, 704
—, —, — pinene, 645
—, —, pyrolysis of aliphatics, 153, 180, 189, 218
—, —, — olefins, 76, 77, 79, 172
—, —, — pinene, 88
—, —, reaction of acetyl chloride and ethylene dichloride, 501
—, —, — carbon and hydrogen, 1278
—, —, — hydrogen bromide and allyl bromide, 315
—, —, — methane and steam, 272
—, —, reduction of carbon dioxide, 1242
—, —, — carbon monoxide, 1223-1225, 1228, 1229, 1231, 1233, 1241, 1249
—, —, — nitroethane, 1094
—, —, sulphation of ethylene, 323
—, effect on decomposition of carbon tetrachloride, 730
—, reaction with sulphur, 1157
—, — trichloroethylene, 711
—, refining agent for gasoline, 668
—, stabilizer, for ether, 335, 337
Iron acetate, catalyst, hydration of acetylene, 714
Iron acetylacetonates, catalysts, phenylcyclopentane autoxidation, 907
Iron alloys, inhibitors, decomposition of ethylene oxide, 554
Iron antimonide, catalyst, dehydrogenation of *sec*-alcohols, 419
Iron arc, action on acetylene, 264
Iron arsenide, catalyst, dehydrogenation of *sec*-alcohols, 419
Iron bismuthate, catalyst, dehydrogenation of *sec*-alcohols, 419
Iron boro-phosphate, catalyst, hydration of ethylene, 285
—, —, — propene, 292
Iron carbonate, catalyst, methane-steam reaction, 278
Iron carbonyl, as antiknock, 1017, 1018
—, catalyst, reaction of phthalic anhydride and carbon monoxide, 950
—, effect on inflammability limits, 985
—, reaction with tetralin peroxide, 906
Iron chloride, catalyst, alkylation of alcohols, 606
—, —, cracking, 112
—, —, ethylation of amines, 347
—, —, polymerization of olefins, 203, 204, 636, 665
—, —, reaction of paraffins and nitrosyl chloride, 1102
—, desulphurizing agent, 488
—, refining agent for petroleum, 719, 928
Iron compounds, catalyst, chlorination of acetylene-hydrogen mixtures, 710
—, —, ethylene-sulphuric acid reaction, 323
—, effect on color stability, 938
—, *see also* Ferric and Ferrous compounds
Iron cyanide, catalyst, sulphation of isobutene, 391
—, —, — propene, 358
Iron fluoride, catalyst, reaction of propene and hydrogen fluoride, 307

Iron halides, catalyst, cracking, 198
—, —, hydration of acetylene, 712
—, —, pyrolysis of hydrocarbons, 158
—, —, reaction of olefins and carbon monoxide, 625
Iron hydroxide, catalyst, reaction of methane and steam, 278
—, —, — sulphur and hydrocarbons, 467
—, for sulphur removal, 459, 1249
Iron iodide, catalyst, reaction of acetone and phenylnaphthylamine, 429
Iron naphthenate, as wetting agent, 1117
Iron ore, for hydrogen sulphide removal, 460
Iron oxide, catalyst, acetone formation, 423
—, —, cracking, 128, 137
—, —, decarboxylation of phthalic anhydride, 951
—, —, dehydration of alcohols, 331
—, —, dehydrogenation of alcohol, 337
—, —, dipropyl ketone from *n*-butyl alcohol, 443
—, —, ethyl alcohol from ether, 334
—, —, ethylation of amines, 347
—, —, hydration of acetylene, 714
—, —, — ethylene, 291
—, —, oxidation of aromatics, 942, 945, 950
—, —, — of ethyl alcohol, 423
—, —, — hydrogen sulphide, 460
—, —, — methyl alcohol, 878
—, —, polymerization of acetylene, 704
—, —, — butadiene, 674
—, —, — olefins, 665
—, —, reaction of ethyl alcohol and steam, 421, 422
—, —, — methane and steam, 278
—, —, — phthalic anhydride and carbon monoxide, 950
—, —, — sulphur and hydrocarbons, 467
—, —, reduction of carbon monoxide, 1229, 1231
—, desulphurizing agent, 23, 1248, 1249
—, effect on ignition temperature, 1000
—, magnetic, catalyst, pyrolysis of hydrocarbons, 157, 192
Iron phosphate, catalyst, hydration of ethylene, 287
—, —, —, propene, 292
—, —, reaction of ethers and alkyl halides, 345
Iron phosphide, catalyst, dehydrogenation of *sec*-alcohols, 419
Iron salts, catalysts, acids from alcohols, 1051
—, —, oxidation of hydrogen sulphide, 461
—, —, — toluene, 950
—, —, polymerization of olefins, 929
—, —, sulphation of isoolefins, 308
Iron selenide, catalyst, dehydrogenation of *sec*-alcohols, 419
Iron sulphate, catalyst, ethylation of amines, 347
—, —, sulphation of propene, 358
Iron sulphide, desulphurizing agent, 397
Iron telluride, catalyst, dehydrogenation of *sec*-alcohols, 419
Iron vanadate, catalyst, oxidation of anthracene, 952
Isethionic acid, condensation with oleic acid, 1082
—, from carbyl sulphate, 1081
Isoacids, from isoaldehydes, 889
Isoaldehydes, oxidation of, 889
Isoamyl alcohol, as antiknock, 1017
—, in motor fuel, 1035
—, octane number of, 1028
Isoamylbenzene, from sapropelite tar, 144
Isoamyl bromide, from amylene, 513
Isoamyl chloride, reaction with anthracene, 827
—, — magnesium, 823
Isoamylcyclopentane, pyrolysis of, 91
Isoamylene, from amine nitrates, 623
—, from dimethylaniline, 623
—, reaction with sulphuric acid, 412
—, — thymol, 606
—, *see also* Isopropylethylene, 2-Methyl-2-butene and Trimethylethylene
Isobar, definition of, 1307
Isobutane, acetylene from, 66, 67, 166
—, chlorination of, 752
—, ethylene from, 67
—, from *n*-butane, 201
—, —, entropy change, 1282
Isobutane, from *n*-butane, free energy change, 1282
—, —, heat of reaction, 1282
—, from cyclohexane, 205
—, from ethylene, 637
—, from *n*-hexane, 201
—, from natural gas, 22
—, heat of combustion, 15
—, ignition temperature of, 992
—, inhibitor, decomposition of ethylene oxide, 554
—, in petroleum, 21
—, isobutene from, 66
—, isooctane from, 1301
—, nitration of, 1088
—, propene from, 66
—, pyrolysis of, 65-67, 148, 555
—, reaction with cyclopropane, 602
—, — ethylene, 599, 601
—, — isobutene, 599
—, — isobutene, free energy change, 1301
Isobutene, acetylene from, 84
—, anthracene from, 85
—, benzene from, 85
—, butadiene from, 85, 86
—, *ter*-butyl alcohol from, 386, 390, 391
—, —, free energy change, 1303
—, *ter*-butyl mercaptan from, 463
—, *ter*-butylsulphuric acid from, 308
—, diisobutylene from, 386, 1300
—, effect on polymerization of *n*-butene, 642
—, ethylene from, 85
—, free energy of formation, 1284
—, from cyclohexane, 92
—, from gas oil, 140
—, from isobutane, 66
—, from isopentane, 69
—, from 2-isopropyl-3,3-dimethyl-1-butene, 411
—, from methylcyclopentane, 90
—, from neopentane, 69
—, from tetramethylpentanol, 401
—, hydration of, 294-297
—, —, free energy change, 296, 1303
—, —, heat of activation, 295
—, isobutenediamine from, 619
—, isobutene glycol from, 895
—, isooctane from, 1300, 1301
—, molal entropy, 1291
—, naphthalene from, 85
—, nitration of, 622
—, oils from, 85, 210
—, oxidation of, 622
—, polymerization of, 210, 296, 390, 633, 641-643
—, —, free energy change, 1300
—, propane from, 84
—, propene from, 85
—, pyrolysis of, 84, 85, 184
—, reaction with benzene, 591, 594, 596
—, — *ter*-butyl hypochlorite, 518
—, — chlorine, 508
—, — 1,3-dimethoxybenzene, 606
—, — ethylene glycol, 544
—, —, hydrogen bromide, 317
—, reaction with isobutane, 599
—, —, free energy change, 1301
—, reaction with isopropyl alcohol, 607
—, — methoxy toluene, 605, 606
—, — sulphur dioxide, 618
—, — sulphuric acid, 308, 385, 386, 391, 1142
—, separation from *n*-butene and butadiene, 386
—, toluene from, 85
—, triethylethylene from, 85
—, triisobutylene from, 591
Isobutene chloride, chlorobutenes from, 508
—, hydrolysis of, 798
Isobutene chlorohydrin, from isobutene, 518, 520
Isobutenediamine, from isobutene, 619
Isobutene glycol, from isobutene, 547, 895
Isobutene nitrosite, preparation of, 620
Isobutene oxide, in adhesives, 586
—, reaction with alcohols, 548, 589
—, — dibenzylamine, 589
Isobutene polymers, motor fuel from, 1040
—, uses of, 674, 675

Isobutyl alcohol, as antiknock, 1017, 1018
—, in motor fuels, 375
—, octane number of, 1028
—, reaction with phenol, 403
—, — ricinoleic acid, 1086
Isobutylbenzene, from sapropelite tar, 144
Isobutyl bromide, dimethylethylene from, 806
—, hydrolysis of, 799
Isobutyl chloride, reaction with phenanthrene, 827
Isobutyraldehyde polymers, motor fuel from, 1040
Isobutyric acid, from isopropylethylene glycol, 548
—, from propene, 626
Isochore, definition of, 1307
Isochloroprene, preparation of, 707
Isohexane, detonation of, 1017
—, from carbon monoxide and hydrogen, 1243
—, from *n*-hexane, 199
Isohexanol, reaction with phenol, 403
Isomerization, of butenes, 81, 82, 642
—, of cyclohexane, free energy change, 1301, 1302
—, of cyclopropane, 90
—, of cyclopropene, 88
—, of *n*-hexane, 200
—, of *n*-hexene, 87, 643
—, of methylacetylene, 88
—, of methylallene, 88
—, of pentenes, 86
Isomorphism, definition of, 422
Isonitroparaffins, preparation of, 1092
Isonitrosoethyl methyl ketone, preparation of, 452
Isononane, in petroleum, 33
Isooctane, as antioxidant, 875
—, as motor fuel, 97
—, from isobutane, 1301
—, from isobutene, 1300, 1301
—, from *n*-octane, 199
—, from petroleum, 32
—, ignition temperature of, 991, 992
—, reference standard in knock rating, 141, 1025-1027
Isooctenyl aldehyde, from butyraldehyde, 878
Isooctylhydrindene, naphthalene from, 94
Isoolefins, as antiknocks, 417
—, polymerization of, 204
—, reaction with sulphuric acid, 308
Isoparaffins, free energy of formation, 1281, 1282
—, in brown coal paraffins, 38
—, in petroleum, 31, 32
—, molal entropy, 1281, 1282, 1289
—, —, effect of structure on, 1288, 1289
—, uses of, 674
Isopentadecane, chlorination of, 1253
Isopentane, diisoamyl ketone from, 445
—, from carbon monoxide and hydrogen, 1243
—, from ethylene and propane, 601
—, from *n*-pentane, 201, 445
—, from petroleum, 21
—, inflammability limits of, 980, 981
—, in motor fuels, 1017
—, pressure-volume-temperature relations, 1322
—, pyrolysis of, 67-69
—, reaction with carbon monoxide, 446
—, — ethylene, 599
—, — phenols, 604
Isophthalic acid, from 1,1,4-trimethylcycloheptene, 94
Isoprene, from dimethylallene, 88, 650
—, from kerosene, 144, 171
—, from 1-methylcyclohexene, 93, 172
—, from pinene, 88
—, from sapropelite tar, 144
—, reaction with *ter*-butyl hypochlorite, 518
—, — chlorine, 686
—, — hydrogen sulphide, 463
—, — maleic acid, 945
—, *see also* 2-Methylbutadiene
Isopropanol, *see* Isopropyl alcohol
Isopropanolamines, preparation of, 587
Isopropenylacetylene, reaction with hydrochloric acid, 721
Isopropyl acetate, from diisopropyl ether, 377
—, from isopropyl alcohol, 376, 1080, 1081
—, from propene, 307
Isopropylacetylene, from dimethylallene, 88
Isopropyl acid sulphate, hydrolysis of, 325
—, preparation of, 359
Isopropyl alcohol, absorption of X-rays by, 367
—, acetic acid from, 371
—, acetone from, 370, 375, 420, 878
—, azeotropic mixtures of, 364, 368, 369
—, dehydration of 173, 364, 365, 420
—, dehydrogenation of, 420, 878
—, 1,3-dimethylbutadiene from, 173
—, electrical properties of, 367
—, estimation of, 370, 371
—, extraction agent, acetic acid, 380
—, —, olefins, 163
—, —, oxygenated hydrocarbons, 975
—, —, α-polyprene, 681
—, —, sulphonates, 1070, 1071
—, free energy of hydration, 368
—, from acetone, 431
—, from isopropyl esters, 356
—, from propene, 288, 291-293, 356-360, 362-364, 366, 895
—, impurities in, 371-373
—, in insecticides, 1078
—, in motor fuels, 369, 370, 1035
—, in rubber cement, 374
—, in varnish removers, 433
—, octane number of, 1028
—, oxalic acid from, 371
—, oxidation of, 370, 371
—, physical properties of, 366, 367
—, polymerization of, 365
—, propene from, 173, 365
—, reaction with acetic acid, 376, 1080, 1081
—, — anisole, 403
—, — benzene, 382, 383, 401, 402
—, — benzoic acid, 376
—, — calcium chloride, 370
—, — chloroacetic acids, 376
—, — ethylene oxide, 557
—, — isobutene, 607
—, — *p*-nitrotoluene, 382
—, — phenol, 402, 403
—, — potassium bromide, 377
—, — toluene, 382, 401, 402
—, — zinc chloride, 370
—, separation from isopropyl ether, 378
—, solvent properties of, 370, 375, 568
—, surface tension of, 366
—, thermal conductivity of, 367
—, utilization of, 372-375
Isopropylamine, preparation of, 428
Isopropylanisole, preparation of, 403
Isopropylbenzene, from isopropyl alcohol, 401
—, from sapropelite tar, 144
—, polymerization of, 208
—, reaction with *ter*-butyl alcohol, 412
—, *see also* Cumene
Isopropyl bromide, from isopropyl alcohol, 377
—, from propene, 306, 307, 316
—, hydrolysis of, 378
—, isomerization of, 316
Isopropyl-*ter*-butylbenzene, preparation of, 412
Isopropyl-*ter*-butyl ether, preparation of, 607
Isopropyl chloride, from propene, 306, 307
—, hydrolysis of, 797
—, reaction with *p*-*ter*-butyltoluene, 816
Isopropylcumyl ether, preparation of, 402
2-Isopropyl-3,3-dimethyl-1-butene, preparation of, 411
Isopropyl esters, preparation of, 375, 376
Isopropyl ether, dewaxing agent for lubricants, 434
—, from propene, 291, 360, 363, 378
—, in motor fuels, 1017, 1030
—, peroxides from, 336, 381
—, separation from isopropyl alcohol, 378
—, solvent for ketene, 437
—, utilization of, 378-380
Isopropylethylene, polymerization of, 203, 377, 378
—, reaction with hydrogen chloride, 310
—, sulphation of, 309
—, *see also* Isoamylene
Isopropylethylene glycol, from amylene, 548
—, isobutyric acid from, 548

Isopropyl hydroperoxide, acetone from, 382
—, from diisopropyl sulphate, 381
—, properties of, 382
Isopropyl-2-hydroxy-3,5-diisopropylbenzoate, preparation of, 308
Isopropyl iodide, from propene, 316, 317
Isopropyl mercaptan, from propene, 462
Isopropylmethylethylene, from di-*ter*-butylethylene, 87
Isopropylnaphthalenesulphonic acid, as wetting agent, 954
N-Isopropyl-α-naphthylamine, preparation of, 429
Isopropylphenol, preparation of, 403
Isopropylphenyl ether, isomerization of, 403
N,N-Isopropylphenyl-β-naphthylamine, preparation of, 429
Isopropyl phthalate, as heat-transfer medium, 377
Isopropyl salicylate, from propene, 308
Isopropyl sulphate, from propene, 363
—, hydrolysis of, 363, 364
Isopropylsulphuric acid, from propene, 305
Isopropylurea, reaction with trihydroxyethyl sorbite, 587
Isoquinoline, from cottonseed meal, 840
Isotherm, definition of, 1307
Isothiocyanates, extraction agents, 44
Isoundecenoic acid, reaction with hydrogen bromide, 318

K

Kaolin, catalyst, dechlorination of propyl chloride, 805
—, —, acetylene from methane, 54
—, in emulsifying agents, 1074
—, in nitric oxide-paraffin reaction, 1091
—, removal of sulphur compounds by, 398
Kattwinkel's reagent, definition of, 1150
—, reaction with aromatics, 1150
—, — unsaturates, 1150
Kauri-butanol test, 1179, 1180
Kero bases, from cottonseed meal, 840
Kerosene, absorbent for butadiene, 174
—, acetaldehyde from, 860, 946
—, acetic acid from, 946
—, acetone from, 860
—, acetylene from, 253
—, aromatics in, 36
—, as cleansing agent, 790
—, benzene from, 137
—, butadiene from, 144
—, by cracking rapeseed oil, 136
—, — tars, 135
—, by oxidation of hydrocarbons, 865
—, by polymerization of olefins, 209
—, carbon monoxide from, 272
—, carboxylic acids from, 860
—, characteristics of, 35
—, chlorinated, dehalogenation of, 807
—, color stability of, 925
—, cracking of, 111, 137, 139
—, cyclopentadiene from, 171
—, dehydration of isopropyl alcohol with, 364
—, determination of gum in, 913
—, dimethylketone from, 946
—, distillation of, 1169
—, dodecene in, 145
—, effect of electric arc on, 253
—, ethylene from, 154, 155, 253
—, formaldehyde from, 860, 946
—, formic acid from, 860, 946
—, from crude oil, 28
—, hydrogen from, 272
—, hydrogen sulphide removed from, 457
—, illuminating power of, 35
—, in demulsifying agents, 1075
—, in motor fuels, 1039
—, in insecticides, 978, 1078
—, isoprene from, 171
—, naphthenes in, 36
—, oxidation of, 859, 860, 946, 965, 966, 1046, 1047
—, piperpylene from, 171
—, pyrolysis of, 154, 155, 195
—, reaction with steam, 272
Kerosene, refining of, 35, 925
—, smoke test, 1184
—, toluene from, 137
—, tridecene in, 145
—, undecene in, 145
—, voltolization of, 261
Kerosene distillates, aviation lubricants from, 211
—, sulphonic acids from, 1076
Ketals, formation of, 722, 723
Ketene, acetylation of alcohols by, 438
—, — benzene by, 439
—, cyclobutane-1,3-dione from, 441
—, decomposition of, 437
—, from acetic acid, 436
—, from acetic anhydride, 436
—, from acetone, 425, 434, 441
—, polymerization of, 440, 441
—, reaction with acetic acid, 435
—, — alcohols, 438
—, — aromatic aldehydes, 438, 439
—, — ethanethiol, 438
—, — 2-ethoxyethanol, 435
—, — haloamines, 440
—, — hydrogen chloride, 439
—, — hydroxy acids, 438
—, — mandelic acid, 439
—, — mercaptobenzothiazole, 439
—, — thioalcohols, 438
—, solvents for, 435
Keto-acids, from petroleum distillates, 843
—, preparation of, 1053
Ketomenthene, preparation of, 895
3-Keto-*n*-pentanol-1, preparation of, 565
Ketones, addition products with nitric acid, 851, 852
—, as antiknocks, 1018
—, as dewaxing agents, 453
—, as extraction agents, 44, 972
—, as solvents, 419, 453
—, by irradiation of petroleum oils, 268
—, by oxidation of alcohols, 406
—, — asphalt, 1203
—, — hydrocarbons, 865, 962-965
—, — petroleum distillates, 843, 856, 1050, 1053, 1056
—, condensation with aldehydes, 443
—, drying of, 443
—, effect on stability of naphthenes, 937
—, electrolytic reduction of, 452
—, formation during aquolysis, 131
—, from butane, 874
—, from carbon monoxide and hydrogen, 1223, 1244
—, from cyclo-olefins, 895
—, from ethyl acetate, 423
—, from naphtha oxidation, 876
—, from nitrocycloparaffins, 1095
—, from paraffin wax, 971
—, from pinacol, 536
—, from primary alcohols, 421
—, from propane, 862
—, from wax acids, 979
—, from secondary alcohols, 399, 419
—, from water gas, 268
—, in synthesis of resins, 419, 453
—, oxidation of, 450
—, photochemical decomposition of, 448-450
—, reaction with 1,2-glycols, 582
—, — mercaptans, 474
—, — zinc halides, 452
Kieselguhr, catalyst, absorption of ethylene, 163
—, —, alkylation of phenols, 605
—, —, isomerization of propene oxide, 586
—, —, reaction of ethylene and cracked gasoline, 1252
—, promoter, reduction of carbon monoxide, 1229, 1230, 1232, 1235, 1239, 1242, 1249
—, use in storing acetylene, 171
Knock-inducing compounds, separation of, 1033
—, effect on ignition temperature, 996
Knock rating, effect of aliphatics, 1024, 1025
—, — argon, 1011, 1012
—, — aromatics, 1024, 1025
—, — cyclohexane derivatives, 1024, 1025
—, — cycloparaffins, 1024, 1025

Knock rating, effect of cyclopentane, 1024, 1025
—, — cyclopentene, 1024, 1025
—, — helium, 1011, 1012
—, — hydrocarbon structure, 1024, 1025, 1027, 1028
—, — lead tetraethyl, 1031-1033
—, — temperature, 1030
—, — type of gasoline, 1033
—, *n*-heptane as reference standard, 1025, 1026, 1027
—, isooctane as reference standard, 1025, 1026, 1027
—, measurement of, 1023-1027, 1029
—, of aviation fuel, 1027
—, of 1-heptene, 1026, 1027
—, *see also* Aniline equivalent
—, *see also* Octane number
Knowles process, for petroleum coke, 230
Kogasin, acids from, 1255
—, action of aluminum chloride on, 1253, 1254
—, aromatics from, 1252
—, as Diesel fuel, 1253
—, chlorination of, 1253
—, composition of, 1224, 1242-1245
—, cracking of, 1252, 1253
—, definition of, 117, 1224
—, dichlorinated, polymerization of, 814
—, gasoline, octane number of, 1251
—, hydrogenation of, 1245
—, in candles, 1255
—, isopentadecane from, 1253
—, lubricating oils from, 1253, 1254
—, olefins from, 1252
—, oxidation of, 1255
—, polymer gasoline from, 1255
—, polymerization of, 1255
—, pyrolysis of, 73, 177
—, separation of paraffin wax from, 1245
—, synthesis of, 214, 1223
Kogasin II, definition of, 131
—, chlorination of, 815
—, electrical cracking of, 131
—, pyrolysis of, 155
Kogasin process, economics of, 1255
Kogasin synthesis, application of, 1245-1255
—, catalysts, preparation of, 1230, 1231, 1232
—, control of temperature, 1233, 1234
—, design of catalyst chambers, 1233, 1234
—, effect of ammonia, 1236
—, — carbon dioxide, 1235, 1241, 1242
—, — carbon disulphide, 1236
—, — composition of feed gas, 1235, 1236
—, — contact time, 1236, 1237
—, — hydrogen sulphide, 1236
—, — methane, 1235
—, — nitrogen, 1235
—, — pressure, 1232, 1233
—, — recycling, 1237-1240
—, — sulphur, 1236
—, — temperature, 1233
—, — time factor, 1237, 1244
—, single-stage process, 1239
—, two-stage process, 1238, 1239
—, three-stage process, 1239, 1240
Kontakt, definition of, 1077
—, as insecticide, 1077
Krypton, effect on acetylene polymerization, 267

L

Lacquers, asphalt in, 1192
—, wax acids in, 975
Lacquer solvents, nitroparaffins as, 1098
Lactic acid, as decolorizing agent, 958
—, by oxidation of wax, 971
—, from carbohydrates, 443
—, from *α*-chloroethyl methyl ketone, 451
—, reaction with butanol-2, 405
Lactides, by oxidation of wax, 971
Lactones, by oxidation of petroleum distillates, 963
—, — naphtha, 876
—, — wax, 971
—, from olefinic acids, 627
Lampblack, dispersion of, 247
—, in printing ink, 250
—, manufacture of, 235, 242
Lamp oil, from carbon monoxide and hydrogen, 1250
Lanthanum oxide, catalyst, dehydrogenation of alcohol, 337
—, —, oxidation of aromatics, 942
—, —, oxidation of methyl alcohol, 878
Lard oil, in anti-rust compositions, 577
—, in brake fluids, 539
Latent energy, in flame gases, 1007
Latex, ethylenediamine stabilizer for, 809
Lauryl diethylene glycol, reaction with chlorosulphonic acid, 545
Lauryl diethylene glycol sulphate, ammonium salt of, 545
Lead, alloys of, use in cracking, 113
—, catalyst, chlorination of benzene, 778
—, —, — toluene, 793
—, —, dehydrogenation of alcohols, 419
—, —, oxidation of aromatics, 942
—, —, — ethylene, 552
—, —, — petroleum oils, 932, 964, 1195
—, —, pyrolysis of olefins, 185
—, —, — paraffins, 160, 257
—, —, sulphation of propene, 360
—, effect on sludge formation, 939
—, estimation in greases, 1165
—, reaction with hydrocarbons, 255, 256
Lead acetate, for hydrogen sulphide detection, 466, 1125
—, reaction with triethanolamine, 571
Lead alkyls, as antiknock agents, 829, 1018
—, preparation of, 255, 256, 1102
Lead borate, catalyst, pyrolysis of paraffins, 160
Lead chloride, catalyst, iodination of cyclohexene, 774
—, —, polymerization of olefins, 665
Lead chromate, catalyst, hydrogenation of sulphur compounds, 1248, 1249
—, —, oxidation of toluene, 948
Lead compounds, catalyst, pyrolysis of pinene, 905
—, effect on ignition temperature of oils, 938
Lead derivatives, catalysts, oxidation of toluene, 947
Lead dimethyl, as antiknock, 1018
Lead dimethyldiamyl, as antiknock, 1018
Lead dioxide, catalyst, oxidation of methane, 867
—, —, — petroleum oils, 1050
—, for color stability of kerosene, 925
Lead fluoride, use in fluorination, 734, 737
Lead halides, catalyst, dehydrogenation of hydrocarbons, 158
—, —, reaction of olefins and carbon monoxide, 625, 626
Lead mahogany sulphonate, in lubricants, 1079
Lead mercaptides, hydrolysis of, 471
—, preparation of, 471
—, reaction with hydrogen peroxide, 475
—, — potassium permanganate, 475
Lead molybdate, catalyst, oxidation of toluene, 948
Lead naphthenate, as antioxidant, 937
—, as drying agent, 1115
—, as wetting agent, 1117
—, in lubricants, 1116
—, in paints, 1115
Lead nitrate, effect on naphthenic acid salts, 1115
Lead oleate, catalyst, oxidation of pinene, 905
Lead oxide, catalyst, decarboxylation of phthalic anhydride, 950, 951
—, —, esterification of pentaerythritol, 1055
—, —, oxidation of aromatics, 942
—, —, — olefins, 553
—, effect on ignition temperature, 1000
—, from lead sulphide, 476
—, from spent doctor solution, 476
—, reaction with *β*,*β*-dichlorodiethyl ether, 579
—, — trimethylene bromide, 547
—, sweetening agent, 476
Lead phosphate, catalyst, hydration of ethylene, 287
Lead sodium alloy, use in gasoline chlorination, 755

Lead sucrate, antioxidant, 917
Lead sulphate, catalyst, ethylene-sulphuric acid reaction, 323
—, —, propene-phosphoric acid reaction, 358
—, —, propene-sulphuric acid reaction, 358
—, promoter, hydration of propene, 292
Lead sulphide, lead oxide from, 476
—, sweetening agent, 475, 476
—, use in refining oils, 1044
Lead susceptibility, definition of, 1031
—, effect of disulphides, 480, 481, 1031
—, — hydrocarbon structure, 1032
—, — thioethers, 1031
Lead tetra-alkyls, reaction with phenol, 823
Lead tetraethyl, as antiknock, 1013, 1017-1022, 1251
—, catalyst, oxidation of naphtha, 876
—, effect, on acetylene homologues, 1019-1021
—, — aromatics, 1019, 1021, 1022
—, — cyclohexane, 1022
—, — cyclopentane, 1022
—, — diolefins, 1019, 1020, 1022
—, — fuels, 916
—, — ignition temperature, 992, 994
—, — knock rating, 1031-1033
—, — olefins, 1019, 1021, 1022
—, — oxidation of benzene, 944
—, — oxidation of gasoline, 861, 947
—, — paraffins, 1019
—, estimation in gasoline, 1165, 1166
—, preparation of, 823
—, reaction with phenol, 823
—, reducing hazards of, 829
—, thermal decomposition of, 1022, 1023
Lead tetramethyl, photolysis of, 1022
Lead tetraphenyl, decomposition of, 1022
—, photolysis of, 1022
Lead tungstate, catalyst, oxidation of toluene, 948
Lead vanadate, catalyst, oxidation of toluene, 948
Leather solvents, preparation of, 825
Le Chatelier's principle, application of, 101
Lecithin, from soy beans, 728
—, from corn, 728
Lepidine, from cottonseed meal, 840
Leucocytosis, effect of cyclopropane, 1268
Leucoindophenol, gum inhibitor, 913
Lewis process, for carbon black, 240
Light, effect on carbene precipitation, 1193
—, — chlorination of methane, 726
—, — gasoline, 924
—, — paraffin-nitrosyl chloride reaction, 1101
Lignin, reaction with ethylene oxide, 559
—, source of petroleum, 19
Lignite, adsorbent carbon from, 227
—, chlorination of, 227
—, inhibitor of gum formation, 914
—, motor fuel from, 136
—, use in cracking, 111
Lignite spirits, refining of, 928
Lime, dehydrating agent, 328, 330
—, catalyst, pyrolysis of oxygenated hydrocarbons, 340
—, use in purification of acetylene, 170
Limonene, reaction with formaldehyde, 624
Liquefaction, of ketene, 441
—, of olefins, 161
Liquid air, determination of acetylene in, 702
Lithia, catalyst, pyrolysis of oxygenated hydrocarbons, 340
Lithium alkyls, as antiknocks, 1018
Lithium aryls, as antiknocks, 1018
Lithium chloride, reaction with triethanolamine, 572
Lithium oleate, catalyst, oxidation of petroleum, 964
Lithium sulphate, promoter, hydration of ethylene, 283
Liver, effect of chloroform on, 1262
—, effect of ethylene on, 1262
Loading value, definition of, 221
Locke's solution, definition of, 1269
Long residium, definition of, 37
Lubricants, aluminum naphthenate in, 1116
—, amylene dichloride in, 513
—, asphalt emulsions in, 1220
Lubricants, antioxidants for, 933, 937, 938
—, artificial aging of, 930
—, by polymerization of olefins, 212-215
—, calcium soaps in, 1079
—, decreasing oiliness of, 935
—, dichlorobenzene in, 790
—, estimation of asphalt in, 1191
—, extraction with chlorinated ethers, 529, 530
—, from chlorinated paraffins, 813
—, — paraffin wax, 757, 758, 817
—, from ethylene glycol esters, 540
—, from glycol ethers, 544
—, from polyglycols, 545
—, from 1,2,4-trichlorobenzene, 790
—, formation of asphaltenes in, 930
—, — carbon in, 930, 931
—, — sludge in, 937
—, graphite in, 1079, 1116
—, increasing viscosity of, 815, 1056
—, lead mahogany sulphonates in, 1079
—, lead naphthenate in, 1116
—, mahogany sulphonates in, 1077
—, nitroparaffins in refining of, 1098
—, oxidation number of, 931
—, oxidation of, 931-933, 935
—, resins from, 1189
—, sludge value determination, 934
—, stability of, 938
—, stabilization of, 937
—, sulphur in, 1116
—, sulphurized, preparation of, 469
—, tests for stability of, 932, 933, 934
—, viscosity determination of, 1172-1176
Lubricating oils, aging of, 931
—, aromaticity of, 44
—, asphaltenes from, 855
—, autoxidation of, 930
—, bloom agent for, 215
—, by polymerization of olefins, 212-215, 671, 672
—, carbenes from, 855
—, chlorination of, 756
—, color determinations of, 1163, 1164
—, depression of pour point, 215
—, dewaxing of, 216, 373, 379, 380, 433, 453, 507, 513, 710, 744, 745, 758, 1044
—, distillation curves of, 1170
—, effect on ignition temperature, 998
—, estimation of acidity, 1166, 1167
—, from crude oil, 28
—, from Kogasin, 815, 1253, 1254
—, hydrocarbons in, 36-38
—, hydroxy acids from, 855
—, increase of film strength, 1055
—, naphthalene in, 36
—, naphthenic acids in, 1103
—, oxidation of, 855
—, preparation from paraffins, 813, 814
—, reaction with amyl chloride, 812
—, refining, with chloroaniline, 46
—, solvent extraction of, 41-45
—, sulphonaphthenic acid salts in, 1118
—, use in demulsifying agents, 1116
—, — insecticides, 1078
—, wax acids in, 978, 979

M

Machine oil, resins from, 1188
Magnesia, catalyst, higher alcohols from ethyl alcohol, 339, 340
—, —, pyrolysis of indenes, 95
Magnesite, catalyst, pyrolysis of olefins, 189
—, —, reduction of carbon monoxide, 1241
Magnesium, catalyst, reaction of acetone and ethyl alcohol, 443
—, promoter, reduction of carbon monoxide, 1228-1230, 1242
—, reaction with 9-bromo-phenanthrene, 824
—, — butyl chloride, 823
—, — chlorinated gasoline, 755
—, — ethylene dibromide, 505, 824
—, — isoamyl chloride, 823
Magnesium alkyl halides, preparation of, 822-824

Magnesium alkylsulphonates, surface tension of, 1066, 1067
Magnesium amalgam, catalyst, condensation of acetone, 427
Magnesium antimonide, catalyst, dehydrogenation of *sec*-alcohols, 419
Magnesium arsenide, catalyst, dehydrogenation of *sec*-alcohols, 419
Magnesium bismuthate, catalyst, dehydrogenation of *sec*-alcohols, 419
Magnesium boro-phosphate, catalyst, hydration of ethylene, 285
—, —, — propene, 292
Magnesium bromide, absorption of ethylene oxide with, 557
—, solubility in isopropyl alcohol, 370
Magnesium bromide dietherate, preparation of, 505
Magnesium carbonate, catalyst, ketones from ethyl acetate, 423
Magnesium chlorate, catalyst, reaction of cellulose phthalate and propene oxide, 588
Magnesium chloride, absorption of hydrocarbons by, 1123
—, catalyst, hydrolysis of chlorobenzene, 783
—, —, in cracking, 112
—, reaction with ethylene oxide, 560
Magnesium dimethyl, reaction with cyclohexene oxide, 589
Magnesium halides, catalysts, hydration of acetylene, 712
Magnesium hydroxide, catalyst, reaction of ethylene dichloride and sodium sulphides, 499
—, for hydrogen sulphide removal, 457
—, sweetening agent, 475, 477
Magnesium iodide, solubility in isopropyl alcohol, 370
Magnesium naphthenate, catalyst, oxidation of paraffin wax, 971
—, —, — petroleum, 972
—, in inks, 1117
Magnesium nitrate, catalyst, methane-steam reaction, 278
Magnesium nitride, desulphurizing agent, 490
Magnesium oxide, absorption of saponifiable hydrocarbons by, 732
—, catalyst, acetone from ether, 421
—, —, chlorination of propene dichloride, 507
—, —, dehydrogenation of acenaphthene, 955
—, —, dipropyl ketone from *n*-butanol, 443
—, —, ethyl alcohol from ether, 334
—, —, ethylene oxide from ethylene chlorohydrin, 550
—, —, hydrolysis of chlorobenene, 782
—, —, in cracking, 128
—, —, oxidation of aromatics, 942
—, —, polymerization of butadiene, 674
—, —, pyrolysis of 2-butene, 172
—, —, — thiophene, 483
—, —, reaction of methanol and carbon monoxide, 1050
—, —, — methane and steam, 270, 279
—, —, reduction of carbon monoxide, 661
—, effect on ignition temperature, 1000
—, — inflammability limits, 985
Magnesium phosphate, catalyst, hydration of propene, 292
Magnesium phosphide, catalyst, dehydrogenation of *sec*-alcohols, 419
Magnesium pyrophosphate, catalyst, propionaldehyde from propene oxide, 586
Magnesium salt, catalyst, acids from alcohols, 1051
—, —, ethylene oxide from ethylene chlorohydrin, 550
Magnesium selenide, catalyst, dehydrogenation of *sec*-alcohols, 419
Magnesium silicate, catalyst, pyrolysis of benzene, 192
—, emulsifying agent for asphalt, 1220
Magnesium sulphate, catalyst fermentation of sucrose, 547
—, promoter, hydration of ethylene, 283
Magnesium telluride, catalyst, dehydrogenation of *sec*-alcohols, 419
Mahogany acids, as demulsifying agents, 1075
—, as emulsifying agents, 1074
—, extraction with β,β'-dichloroethyl ether, 530
—, in insecticides, 1077
—, solubility of, 1065
Mahogany soaps, in cleaning compositions, 732
Mahogany sodium sulphonate, in cleaning agents, 746
Mahogany sulphonates, extraction with green-acid soap, 1071, 1072
—, — isopropyl alcohol, 1071
—, — propane, 1071
—, utilization of, 1077-1080
Maleic acid, condensation with diolefins, 945
—, from acenaphthene, 946
—, from benzene, 944
—, from cyclohexanone, 451
—, from furfuraldehyde, 945
—, from naphthalene, 946, 951
—, hydration of, 945
—, reduction of, 945
—, *meso*-tartaric acid from, 547
Maleic anhydride, as antioxidant, 941
—, from benzene, 944-946
—, from fluorene, 954, 955
—, reaction with benzol, 690
—, — diolefins, 175, 679, 698, 699, 1147
—, — olefins, 629
Malic acid, from maleic acid, 945
Malonic acid, preparation of, 904
Maltenes, in asphalt, 1197, 1198
Mandelic acid, acetylation of, 439
Manganese, catalyst, acetone from acetaldehyde, 423
—, —, dipropyl ketone from *n*-butanol, 443
—, —, ethers from acetals, 715
—, —, in cracking, 114
—, —, oxidation of ethylene, 553
—, —, — wax, 971, 1057
—, —, pyrolysis of aliphatics, 189
—, —, reaction of carbon disulphide and chlorine, 730
—, —, — methane and steam, 272
—, promoter, chlorination of benzene, 779
—, —, in cracking, 128
—, —, reduction of carbon monoxide, 1228, 1229, 1231, 1234-1236, 1239, 1240, 1243, 1248
Manganese acetate, catalyst, hydration of acetylene, 714
—, —, oxidation of acetaldehyde, 885
—, —, — acetone, 432
Manganese acetylacetonate, catalyst, phenylcyclopentane, autoxidation, 907
Manganese alloys, catalyst, carbon from carbon monoxide, 229
Manganese borate, catalyst, pyrolysis of paraffins, 160
Manganese boro-phosphate, catalyst, hydration of butenes, 293, 294
—, —, — ethylene, 285, 286
—, —, — isobutene, 296
—, —, — propene, 292
Manganese, butyrate, catalyst, oxidation of acetaldehyde, 885
Manganese carbonate, catalyst, oxidation of methane, 881
Manganese chloride, catalyst, chlorination of ethylene, 495
—, —, — propene, 507
—, —, ether from ethyl alcohol, 331
—, effect on naphthenic acid salts, 1115
—, reaction with ethylene oxide, 560
—, — soaps, 1055
Manganese compounds, catalyst, nitration of toluene, 954
—, —, oxidation of *d*-α-pinene, 905
—, effect on color stability, 938
Manganese dioxide, absorption of hydrogen sulphide with, 1125
—, catalyst, oxidation of kerosene, 859, 860
—, —, — oils, 1047, 1054
—, —, — sodium sulphide, 465
—, —, pyrolysis of methane, 218, *227*
—, inhibitor, deterioration of ethylene oxide, 554

Manganese dioxide, promoter, in cracking, 112
—, —, pyrolysis of alcohol, 351
—, sweetening agent, 475
Manganese fluoride, catalyst, reaction of propene and hydrogen fluoride, 307
Manganese halides, catalyst, pyrolysis of paraffins, 158
—, —, reaction of dichloroethane and hydrogen fluoride, 747
—, —, — olefins and carbon monoxide, 625, 626
Manganese hydroxide, catalyst, reaction of sulphur and hydrocarbons, 467
—, for hydrogen sulphide removal, 458, 459
Manganese naphthenate, as antioxidant, 937
—, drying agent, 1115
—, promoter, oxidation of paraffin wax, 971
Manganese nitrate, catalyst, oxidation of acenaphthene, 955
Manganese oleate, catalyst, oxidation of paraffin wax, 971
—, —, — petroleum distillates, 962, 1059
—, —, — *d*-α-pinene, 905
Manganese oxide, catalyst, acetone from ethyl alcohol, 421, 423
—, —, chlorination of benzene, 781
—, —, hydration of acetylene, 714
—, —, in cracking, 137
—, —, ketones from ethyl acetate, 423
—, —, oxidation of aromatics, 942
—, —, — butyl alcohol, 880
—, —, — methane, 881
—, —, reaction of ethyl alcohol and steam, 422
—, —, — sulphur and hydrocarbons, 467
—, drying agent for isopropyl alcohol, 420
—, effect on ignition temperatures, 1000
—, in hydrogen sulphide removal, 458
Manganese phosphate, catalyst, hydration of ethylene, 284
—, —, — propene, 292
Manganese propionate, catalyst, oxidation of acetaldehyde, 885
Manganese salts, catalyst, acids from alcohols, 1051
Manganese soap, catalyst, oxidation of oils, 1044
—, —, — paraffin wax, 972
Manganese sulphate, promoter, hydration of ethylene, 283
Manganese vanadate, catalyst, oxidation of anthracene, 952
Mannitol, reaction with butylacetylene, 724
Marine plants, origin of petroleum, 21
Markownikov rule, 298
Mazout, cracking of, 103
—, definition of, 273
—, reaction with steam, 273
—, refining with charcoal, 1188
Medicinal compounds, preparation of, 690, 1080
Mellitic acid, preparation of, 822
Menthane, halogenation of, 776
Menthene, reaction with selenious acid, 446
—, — selenium dioxide, 895
Menthol, dehydrogenation of, 444
—, in motor fuels, 1035, 1039
Menthone, from menthol, 444
—, reaction with nitric acid, 850, 851
Mercaptans, acidity of, 469
—, alkylsulphonic acids from, 1066
—, as antioxidants, 486, 487, 937
—, as odorizing agents, 471
—, detergents from, 487
—, disulphides from, 470, 471, 480
—, emulsifying agents from, 487
—, estimation in gasoline, 1157-1159
—, extraction with alkali, 469, 470
—, from alkyl halides, 822
—, from sulphur, 1157
—, hydrogenation of, 1248, 1249
—, hydrogen sulphide from, 478
—, in fungicides, 487
—, in insecticides, 487, 1112
—, in petroleum, 454
—, oxidation of, 470, 471, 480, 1043, 1066, 1158
—, photochemical decomposition of, 473
—, properties of, 471
—, pyrolysis of, 479
Mercaptans, reaction with acetylene, 472, 473, 715
—, — aldehydes, 473, 474
—, — alkyl halides, 479, 485
—, — cupric chloride, 477
—, — diazotized amines, 479
—, — ethylene chlorohydrin, 526
—, — ethylene oxide, 472, 564
—, — ketones, 474
—, — sodium hydrosulphide, 480
—, — sodium hypochlorite, 470
—, — sodium plumbite, 474, 475
—, — sulphonic acids, 472
—, — sulphur, 470
—, — sulphur chloride, 481
—, — thionylaniline, 481
—, — thionyl chloride, 481
—, removal, by distillation, 470
—, —, from alcohols, 397, 408
—, stabilizing agents for carbon tetrachloride, 730
—, sulphonic acids from, 471
—, thioethers from, 472, 473
—, wetting agents from, 487
Mercaptobenzothiazole, reaction with ketene, 439
Mercuric acetate, reaction with acetylene, 702
—, — cyclohexene, 628
—, — methylcyclohexene, 628
—, — octahydronaphthalene, 628
—, — olefins, 1149-1151
Mercuric bromide, precipitant for asphalts, 1191
—, reaction with mercury dimethyl, 51
Mercuric chloride, catalyst, reaction of acetylene and hydrogen chloride, 716
—, —, — butadiene and methoxybenzylchloride, 698
—, —, — cyclohexadiene and aryl halides, 693
—, —, — cyclohexadiene and chloroethers, 693
—, —, — diolefins and aryl halides, 691
—, —, — propene and hydrogen chloride, 306
—, effect on pyrolysis of methane, 54
—, reaction with acetylene, 702
—, — thioethers, 479
—, — thiophene, 483
—, refining agent for oils, 1044
Mercuric fluoride, reaction with ethyl bromide, 748
Mercuric nitrate, promoter, hydration of isobutene, 295, 296
—, reaction with cyclohexene, 629
—, — ethylene, 629
Mercuric orthophosphate, catalyst, acetylene-acetic acid reaction, 717
Mercuric oxide, catalyst, hydration of acetylene, 712
—, —, reaction of acetylene and acetic acid, 717
—, —, — ethyl alcohol and vinylacetylene, 706
—, —, — mannitol and butylacetylene, 724
—, —, — methyl alcohol and alkylacetylenes, 722
—, refining agent for ether, 336
Mercuric salts, catalyst, nitration of toluene, 954
—, — reaction of vinylacetylene and carboxylic acids, 706
—, reaction with vinylacetylene, 708
Mercuric sulphate, catalyst, reaction of acetylene and acetic acid, 717
—, —, — alcohol, 715
—, —, — ethylacetoacetate, 721
—, —, reaction of vinylacetylene and acetic acid, 706
—, —, sulphation of tetrachloroethane, 829
—, reaction with *ter*-butyl alcohol, 365
Mercuric sulphonate, catalyst, reaction of acetylene and acetic acid, 717
Mercurous fluoride, reaction with butyl iodide, 753
—, — iodoform, 737
—, — bromocyclohexane, 773
Mercury, as heat-transfer medium, 28, 193, 861
—, catalyst, bromination of benzene, 790, 791
—, —, carbon from petroleum coke, 232
—, —, oxidation of petroleum, 964
—, —, pyrolysis of gaseous hydrocarbons, 158
—, —, pyrolysis of olefins, 78
—, promoter, reduction of carbon monoxide, 1229

Mercury, reaction with peroxides, 381
—, — sulphur, 1156, 1162
—, vapor, inhibitor, pyrolysis of methane, 54, 55
Mercury arc, action on acetone, 450
—, — acetylene, 264, 266
—, — bivinyl, 265
Mercury bromide, catalyst, reaction of propene and acetic acid, 308
Mercury chloride, catalyst, reaction of propene and acetic acid, 308
—, —, — vinyl chloride and hydrogen chloride, 716
—, refining agent for gasoline, 929
Mercury compounds, catalyst, hydration of acetylene, 712
Mercury halides, catalyst, dichloroethane-hydrogen fluoride reaction, 747
Mercury oxide, catalyst, oxidation of olefins, 553
Mercury phosphate, catalyst, reaction of propene and acetic acid, 308
—, promoter, hydration of ethylene, 291
Mercury salts, catalyst, hydration of acetylene, 702
—, —, — denterioacetylene, 725
—, —, — vinylacetylene, 705
—, —, reaction of acetylene and acetic acid, 717
—, —, — aromatics, 719
—, —, reaction of ethylacetylene and acetic acid, 718
—, reaction with olefins, 628
Mercury sulphate, catalyst, reaction of propene and acetic acid, 308
—, —, sulphation of propene, 358
Mercury trichloroethylenide, preparation of, 711
Mesitol, from mesitylene, 954
Mesitylene, from acetone, 431
—, from acetylene and toluene, 719
—, from kerosene, 36
—, from sapropelite tar, 144
—, from xylenes, 208
—, oxidation of, 954
—, reference standard in Diesel fuel, 1033
Mesitylenealdehyde, from mesitylene, 954
Mesitylenic acid, from mesitylene, 954
Mesityl oxide, acetone from, 423
—, from acetone, 429, 878
—, from diacetone alcohol, 430
—, reaction with diolefins, 175
—, — ozone, 901
Metal chlorides, catalysts, pyrolysis of amines, 158
—, —, reaction of monovinylacetylene and hydrogen chloride, 680
Metal cyanides, catalyst, reaction of olefins with sulphuric acid, 392
Metal dispersions, in oils, 256
Metal halides, catalyst, alkylation of phenols, 603
Metallocyanic acids, as antiknocks, 1018
Metal naphthenates, catalysts, oxidation of solar oil, 940
Metal nitrides, desulphurizing agents, 490
Metal oxides, catalysts, oxidation of ethylene, 844
—, —, reaction of olefins and carbon monoxide, 626
Metal selenides, as antioxidants, 919
Metal soaps, catalysts, oxidation of paraffin wax, 972
—, emulsifying agents for asphalts, 1216
—, from transformer oil, 935
Metal sulphates, catalyst, reaction of olefins with sulphuric acid, 390
Metal sulphides, as antioxidants, 919
Metal tellurides, as antioxidants, 919
Metal wool, catalyst, polymerization of olefins, 1042
Methacrylic acid, esters, preparation of, 611
Methacrylonitrile, from acetone cyanohydrin, 428
Methanation, of petroleum distillates, 115
Methane, acetaldehyde from, 264, 883
—, acetylene from, 53-55, 165, 166, 168, 218, 254, 255, 257, 892
—, action of electric arc on, 253, 254
—, — glow discharge on, 263
—, — silent discharge on, 257, 263
—, aromatics from, 179, 218
Methane, as fuel, 27, 1017
—, benzol from, 180
—, carbon black from, 255
—, carbon from, 215, 218
—, carbon-hydrogen bond of, 1138
—, carbon monoxide from, 1246
—, carbon tetrachloride from, 726
—, chlorination of, 726-730
—, combustion of, 52, 225, 1003-1005
—, —, mechanism, 1000
—, deasphalting agent, 45
—, dihydroxydimethyl peroxide from, 882
—, effect on chlorination of olefins, 493
—, — decomposition of acetaldehyde, 884
—, — Kogasin synthesis, 1235
—, enthalpy table for, 1337
—, entropy table of, 1337
—, estimation of, 1128, 1129
—, ethane from, 158, 257
—, ethylene from, 53, 158, 166, 218, 257
—, formaldehyde from, 264, 857, 858, 866, 870, 880-883
—, formic acid from, 857, 858, 883
—, free energy of formation, 1225, 1278, 1279
—, from acetone, 425
—, from acetylene, 703
—, from benzene, 95
—, from butane, 62, 201
—, from carbon and hydrogen, 1278
—, from carbon monoxide and hydrogen, 1223, 1235, 1236, 1240-1242
—, from cracking gas, 101, 301
—, from cyclohexane, 93
—, from cyclopentane, 90
—, from cylinder oil, 137
—, from ethyl alcohol, 173, 331, 347-349, 352, 353
—, from ethylbenzene, 96
—, from ethylcyclohexane, 93
—, from ethylene oxide, 554
—, from gas oil, 140
—, from *n*-hexane, 71
—, from isobutene, 84
—, from Kogasin, 131
—, from methyl radical, 75
—, from neopentane, 69
—, from *n*-nonane, 72
—, from *n*-pentane, 68
—, from pentenes, 86, 87
—, from propane, 60, 151, 169
—, from propene, 80
—, from tetradecane, 100, 1297
—, from triacetin, 19
—, hexamethylenetetramine from, 264, 882
—, hydrogen from, 53, 218, 224, 234, 253, 1246, 1247
—, ignition of, 1000, 1001
—, ignition temperature of, 986-988, 992, 993, 995-997
—, inflammability limits of, 983-985
—, inhibitor, decomposition of ethylene oxide, 554
—, in natural gas, 22
—, in petroleum gases, 21
—, methylal from, 867
—, methyl alcohol from, 269, 857, 858, 866, 867, 870
—, methyl chloride from, 726
—, molal entropy, 1288
—, naphthalene from, 180
—, oxidation of, 224, 276, 858, 866-871, 880-883, 1246
—, —, effect of hydrogen and carbon monoxide, 869
—, —, effect of temperature and pressure, 857
—, —, mechanism, 845-849, 995
—, photochemical decomposition of, 267
—, pressure-volume-temperature relations, 1322
—, propane from, 263
—, pyrolysis of, 52-55, 149, 158, 165-169, 180, 216, 218-220, 227, 228, 1017, 1247
—, —, mechanism, 53
—, reaction with ammonia, 280, 281
—, — calcium chloride, 1102
—, — carbon, 168
—, — carbon dioxide, 273-275, 870, 1246

Methane, reaction with nitric oxide, 281
—, — steam, 270-273, 276-279, 870, 1246, 1247
—, removal from gas mixtures, 190, 657, 1133
—, solubility in benzine, 234
—, — oils, 9
Methanol, *see* Methyl alcohol
Methenyl radical, from acetylene, 89
—, from gaseous hydrocarbons, 52
Methoxybenzyl chloride, reaction with butadiene, 698
4-Methoxy-2-butanone, preparation of, 706
2-Methoxy-1,1-dimethylethanol, preparation of, 548
2-Methoxyethanol, trichloroacetyl glycol methyl ether from, 541
Methoxytoluene, reaction with isobutene, 605, 606
Methyl acetate, extraction agent, 44, 380
—, from methyl alcohol, 1050
p-Methylacetophenone, preparation of, 448
1-Methyl-2-acetylcyclopentane, from cyclohexane, 205, 445
Methylacetylene, from propene dibromide, 508
—, from sodium acetylide, 722
—, isomerization of, 88
—, reaction with hydrogen bromide, 723
—, — sodium, 722
Methylacetylide, reaction with methyl iodide, 722
Methylal, from methane, 867
Methyl alcohol, as antiknock, 1016, 1017
—, azeotropic mixture with carbon tetrachloride, 407
—, catalyst, reaction of styrene and hydrogen chloride, 311
—, demulsifying agent, 1158
—, estimation of, 371
—, extraction agent for chloroprene polymers, 681
—, — oils, 495, 1200
—, — olefins, 163
—, — oxidized wax, 975, 977
—, formaldehyde from, 877-879
—, from butane, 863
—, from carbon monoxide and hydrogen, 242, 1049, 1223
—, —, free energy change, 1304, 1305
—, —, mechanism, 1304
—, from ethane, 856-858
—, from methane, 269, 857, 858, 866-868, 870
—, from methyl chloride, 727, 796
—, from natural gas, 862
—, from propane, 862, 863
—, inflammability limits of, 980-982
—, 2-methoxy-1,1-dimethylethanol from, 548
—, methyl hypochlorite from, 626
—, methyl phthalate from, 952
—, oxidation of, 851, 877-879
—, reaction with acetone, 443
—, — alkylacetylenes, 722
—, — butene, 606, 607
—, — carbon monoxide, 1050
—, — chlorine, 626
—, — cyclohexene chlorohydrin, 589
—, — phthalic anhydride, 952
—, — sodium phenolate and carbon monoxide, 957
—, — stilbene and bromine, 514
—, — vinylacetylene, 706
—, solvent for cellulose esters, 507
Methyl alcohol-cyclohexane, extraction agent for resins, 1188
Methyl alcohol-gasoline blend, effect of water on, 1035
Methyl alcohol-phenol, extraction agent for oils, 42
Methylallene, polymerization of, 649, 650
—, pyrolysis of, 88
Methylamine, from nitromethane, 1094
p-Methylamino-*p'*-amino diphenyl ether, as antioxidant, 916
Methyl-*ter*-amyl ether, extraction agent, 418
Methyl amyl ketone, preparation of, 443
Methylaniline, as antiknock, 1018
2-Methylbenzanthrone, oxidation of, 957
Methyl benzoate, from dimethyl phthalate, 952
Methyl bromide, in fire extinguishers, 505
—, reaction with sodium, 826
1-Methyl-2-bromo-1-cyclohexanol, preparation of, 531
1-Methylbutadiene, *see* Piperylene
2-Methylbutane, *see* Isopentane
2-Methyl-1-butanol, preparation of, 901
2-Methyl-2-butanol, from amine nitrate, 623
—, from cracked gasoline, 388
—, *see also* *ter*-Amyl alcohol
2-Methyl-1-butene, from sapropelite tar, 144
—, polymerization of, 203
—, reaction with hydrogen chloride, 310
—, — sulphuric acid, 308
2-Methyl-2-butene, hydration of, 296, 297
—, oxidation of, 901
—, preparation of, 411
—, reaction with aniline, 615
—, — ethylene glycol, 544
—, *see also* Trimethylethylene and Isoamylene
2-Methyl-2-butene nitrosite, preparation of, 620
2-Methyl-1-buten-3-ol, oxidation of, 444
2-Methyl-2-buten-4-ol, oxidation of, 444
Methyl-*ter*-butyl carbinol, dehydration of, 645
Methyl-*sec*-butyl ether, preparation of, 606, 607
Methyl-*ter*-butyl ether, extraction agent, 418
Methyl butyl ketone, decomposition of, 448-450
Methyl chloride, acetyl chloride from, 727
—, as refrigerant, 545, 727, 790
—, chlorination of, 727
—, dewaxing agent, 727, 738, 739
—, from chloroform, 729
—, from dimethyl ether, 794
—, from methane, 726
—, hydrolysis of, 727, 728, 796
—, oxidation of, 849
—, promoter, polymerization of unsaturates, 215
—, reaction with carbon monoxide, 727
—, — formaldehyde, 727
—, stabilization of, 727
—, toxicity of, 727
2-Methyl-3-chloro-1-butene, preparation of, 513
1-Methyl-4-chloro-3-cyclohexanol, preparation of, 521
Methylcyclobutane, reaction with bromine, 763
—, — halogen hydrides, 763
Methylcyclohexadiene, from *n*-butenes, 81
—, from 1-methyl-2-chlorocyclohexanol, 521
Methylcyclohexane, butadiene from, 93
—, cracking of, 111
—, from petroleum, 34
—, from sapropelite tar, 144
—, from toluene, 208
—, halogenation of, 775
—, isomerization of, 206
—, molal entropy, 1290
—, oxidation of, 843
—, pyrolysis of, 91, 93
—, reaction with ethylene, 599
Methylcyclohexanediols, preparation of, 521
Methylcyclohexanol, in motor fuel, 1039
—, octane number of, 1028
—, preparation of, 589
—, reaction with acetic acid, 406
—, — hydrochloric acid, 775
—, — naphthalenesulphonic acid, 410
—, — phosphorus pentachloride, 775
Methylcyclohexene, chlorohydrin from, 521
—, from *n*-butenes, 81
—, oxidation of, 907
—, pyrolysis of, 93, 172
—, reaction with bromine, 775
—, — mercuric acetate, 628
—, — selenious acid, 446
—, — sulphur dioxide, 618
Methylcyclopentadiene, from cracked distillates, 679
Methylcyclopentane, from cyclohexane, 205
—, —, free energy change, 1301, 1302
—, from gasoline, 34
—, methylcyclopentene from, 205, 445
—, pyrolysis of, 89-91
—, reaction with ethylene, 599
Methylcyclopentene, chlorohydrin from, 521
—, from methylcyclopentane, 205, 445
—, reaction with acetyl chloride, 205
1-Methyl-3-cyclopentylformaldehyde, preparation of, 521
Methyl-di-*ter*-butylcarbinol, dehydration of, 411
Methylene blue, adsorption by carbon black, 249
Methylene bromide, preparation of, 53

Methylene chloride, difluoromethane from, 734
—, from methyl chloride, 727
—, hydrolysis of, 728
—, oxidation of, 849
—, properties of, 728
—, reaction with antimony trifluoride, 734
—, — formaldehyde, 728
—, —, pyrocatechol, 828
—, — trimethylene mercaptan, 485
—, toxicity of, 728
—, utilization of, 728, 745
Methylene iodide, preparation of, 53
Methylenepyrocatechol, preparation of, 828
Methylene radical, dimerization of, 53
—, formation of, 50-53
—, reaction with halogens, 53
1-Methyl-1,2-epoxycyclohexene, preparation of, 521
Methylethylacetic acid, esterification of, 407
—, from butane, 1100
Methylethylacetylene, oxidation of, 904
Methylethylbenzene, *see* Ethyltoluene
Methylethylbutyl carbinol, dehydration of, 901
unsym-Methylethylethylene, *see* 2-Methyl-1-butene
Methyl ethyl ketone, deasphalting agent, 1192
—, decomposition of, 448, 449
—, dewaxing agent, 433, 453
—, extraction agent for *m*-dinitrobenzene, 1148
—, — polyprene, 681
—, from acetone and methanol, 443
—, from 2-butene oxide, 588
—, from butenes, 293, 897
—, from *sec*-butyl alcohol, 442
—, from ethylacetylene, 718
—, non-solvent in rubber cement, 374
—, reaction with acetone, 433
—, — amyl nitrite, 452
—, — phosphorus pentachloride, 452
—, solvent for ketene, 435
4-Methyl-3-ethyl-2-pentanone, preparation of, 445
4-Methyl-3-ethyl-3-penten-2-one, preparation of, 445
Methylethylpinacone, reaction with sulphuric acid, 678
Methyl formate, in reaction of acetone and amines, 428
—, preparation of, 1050
α-Methylglutaric acid, from methylcyclopentane, 876
β-Methyl glycerol, preparation of, 523
2-Methylheptane, from ethylene and isobutane, 601
—, from petroleum, 32
2-Methylhexane, from petroleum, 32
Methylhydrindene, pyrolysis of, 94
Methyl α-hydroxyisobutyrate, preparation of, 428
Methyl hypobromite, from methyl alcohol, 514, 531
—, reaction with aromatics, 531
—, — 1,3-cyclohexadiene, 531
Methyl hypochlorite, from methyl alcohol, 626
Methyl iodide, reaction with sodium acetylide, 722
Methyl isobutyl ketone, dewaxing agent, 433, 453
—, solvent for antioxidants, 919
Methylisopropenylacetone, preparation of, 444
Methylisopropylacetone, preparation of, 444
Methylisopropylbenzene, from sapropelite tar, 144
Methylisopropylbicyclononane, cracking of, 137
Methylisopropylethylene, polymerization of, 643, 645
unsym-Methylisopropylethylene, preparation of, 411, 645
Methylisopropylhexahydrofluorene, pyrolysis of, 94
Methyl isopropyl ketone, oxidation of, 450
Methyl mercaptan, preparation of, 526
—, reaction with ethylene chlorohydrin, 526
Methyl methacrylate, preparation of, 428
1-Methyl-3-methoxy-4-*ter*-butylbenzene, preparation of, 416
Methyl morpholine, utilization of, 585
Methylnaphthalene, from petroleum, 36, 40
—, from propane, 182
—, reaction with chlorinated Kogasin, 1253, 1254
Methyl naphthyl ketone, preparation of, 447, 448
Methyl nitrate, decomposition of, 1093
2-Methyl-2-nitropropane, preparation of, 1088
2-Methyl-1-nitro-1-propene, preparation of, 622
3-Methyloctane, from carbon monoxide and hydrogen, 1243
2-Methyl-1,3-octanediol, from 2-octene, 624
Methyl oleate, reaction with ozone, 902
Methylolurea, reaction with ethylene chlorohydrin, 525, 526
2-Methylpentane, from *n*-hexane, 198
—, from petroleum, 32
3-Methylpentane, detonation of, 1017
—, from *n*-hexane, 198
—, from petroleum, 32
2-Methyl-2-pentanol, from gasoline, 389
3-Methyl-2-pentanol, from 2-butene oxide, 588
4-Methyl-2-pentanol, from 4-methyl-2-pentene, 356
2-Methylpentene, from propyl alcohol, 173
2-Methyl-1-pentene, preparation of, 411
—, 2,2-dimethylbutanol from, 388
2-Methyl-2-pentene, oxidation of, 901
—, preparation of, 411
3-Methylpentene, reaction with phenols, 606
3-Methyl-2-pentene, oxidation of, 901
—, polymerization of, 643
—, reaction with aniline, 615
Methylphenol, reaction with propene, 605
Methylphenylacetylene, from benzylacetylene, 807
1-Methyl-3-phenylcyclopentane, from benzene, 207
Methyl phthalate, preparation of, 952
2-Methyl-2-propanol, *see* *ter*-Butyl alcohol
Methylpropene, *see* Isobutene
Methylpropylacetone, *see* 2-Acetylpentane
Methyl propyl ketone, from *sec*-pentanol, 443
—, from 2-pentene oxide, 589
2-Methylpyridine, reaction with aldehydes, 623
Methyl pyromucate, reaction with *ter*-amyl chloride, 818
Methylquinoline, from anthracene oil, 839
Methyl radical, formation of, 51, 52, 55, 79
—, reactions of, 50, 51
2-Methylsulphonyl-1-methylethane-1-sulphonic acid, salt, preparation of, 618
Methyltetrahydropicoline, reaction with formaldehyde, 623
p-Methyltolylbenzol, preparation of, 473
Methyl vinyl ketone, preparation of, 704, 705
Mineral oil, action of aluminum chloride on, 213, 216
—, carcinogenity of, 209
—, dewaxing of, 753
—, effect on ignition temperature, 998
—, ethylene glycol ethers in, 543
—, from petroleum, 28
—, in emulsifying agents, 1079
—, in foam-preventing agents, 1080
—, in insecticides, 1077, 1115
—, in lubricants, 1077, 1116
—, in polishing compositions, 1079
—, in vulcanization of rubber, 1078
—, medicinal products from, 1080
—, naphthenic acids in, 1112
—, oxidation of, 856, 938, 939
—, promoter, ethyl alcohol from ether, 333
—, pyrogenetic origin of, 17
—, refining with acetone, 434
—, — chlorosulphonic acid, 1076
—, solubility of castor oil in, 759
—, sulphonic acids from, 1076
—, wax acids in, 979
Mineral-oil sulphonates, as wetting agents, 1076
—, in detergents, 1086
Molal average boiling point, characterization factor from, 1307, 1309, 1310
—, critical pressure from, 1318
—, critical temperature from, 1312, 1313
—, determination of, 1308, 1309
—, molecular weight from, 1311
Molecular beam, of ethane, 55
Molecular weight, determination of, 1172, 1311
—, heat of vaporization from, 1325, 1327
—, pseudocritical points from, 1318, 1319
Mollier diagrams, determination of, 1341-1343
Molybdenum, catalyst, hydrogenation of olefins, 1154
—, —, in cracking, 114, 134
—, —, oxidation of ethane, 872
—, —, polymerization of acetylene, 705
—, —, pyrolysis of benzene, 191
—, —, — gaseous hydrocarbons, 160, 185, 189
—, —, reduction of carbon monoxide, 1240

Molybdenum, promoter, in cracking, 128
—, —, oxidation of methyl alcohol, 879
—, —, — toluene, 949
Molybdenum carbonate, catalyst, oxidation of methane, 881
Molybdenum halides, catalyst, pyrolysis of aliphatics, 158
Molybdenum oxide, catalyst, alkylation of naphthenes, 603
—, —, in cracking, 115
—, —, methane-steam reaction, 279
—, —, oxidation of aromatics, 942
—, —, — gas oil, 863
—, —, — hydrogen sulphide, 460
—, —, — kerosene, 966
—, —, — methane, 869, 871, 881
—, —, — methyl alcohol, 878
—, —, — petroleum, 844, 1053
—, —, pyrolysis of aliphatics, 74
—, —, — cyclohexane, 92
—, —, — ethylbenzene, 159
—, —, — hexane, 71
—, —, — methane, 228
—, —, — naphthenes, 186
—, —, reduction of carbon monoxide, 661, 1228
Molybdenum sulphide, catalyst, polymerization of hexene, 643
—, —, pyrolysis of heptane, 72
—, —, — 1-hexene, 87
—, —, — octane, 72
Molybdenum trioxide, catalyst, ketone-alcohol reaction, 443
—, —, pyrolysis of thiophene, 483
Molybdenum trisulphide, catalyst, hydrogenation of thiophene, 485
—, —, pyrolysis of thiophene, 483
Molybdic acid, promoter, pyrolysis of alcohol, 351
Molybdic acid salts, catalyst, hydration of ethylene, 288
—, —, oxidation of ethylene, 894
—, —, reaction of olefins and carbon monoxide, 626
Monel metal, catalyst, pyrolysis of butane, 63
—, —, — isobutene, 85
—, —, — olefins, 77
—, —, — propene, 79
—, effect on decomposition of carbon tetrachloride, 730
Monohydric alcohols, glycol dialkyl ethers from, 544
—, reaction with phthalic acid, 542
Montan wax, bleached, preparation of, 1057
Morpholine, properties of, 583
—, structure of, 582, 810
—, utilization of, 584, 810
Morpholineethanol, solvent properties of, 584
Morpholineethyl ether, utilization of, 584, 585
Morpholinevinyl ether, hydrolysis of, 585
Motor benzol, as fuel, 142
Motor fuel, acetylene as, 1040
—, blended, 1034-1040
—, blending agents for, 1039
—, color determinations of, 1163, 1164
—, discoloration prevention, 268
—, from carbon monoxide and hydrogen, 1245
—, from diacetone alcohol, 1040
—, from ethylene-propene mixture, 288
—, from hydrorubber, 1040
—, from isobutene polymers, 1040
—, from isobutyraldehyde polymers, 1040
—, from lignite, 136
—, from petroleum, 97, 865, 964, 1047
—, from polystyrene, 1040
—, from tars, 134-136
—, from vegetable oil, 136
—, from waste rubber, 136
—, olefins as, 1040
—, paraffins as, 1040
—, *see also* Gasoline
Mustard gas, *see* Dichlorodiethyl sulphide
Myristyl halides, glycol ethers from, 543

N

Naphtha, acids from, 881
—, aldehydes from, 881
Naphtha, as solvent, 728
—, cracking of, 139
—, critical pressure of, 1316
—, enthalpy-pressure-temperature relations, 1333, 1334
—, heat content of, 1331, 1332
—, in cleaning agents, 732, 746
—, in decolorizing resins, 216
—, inflammability limits of, 986
—, in polishing compositions, 1079
—, oxidation of, 875, 876, 881, 966, 1046
—, reaction with olefins, 592
—, reforming, 116
—, total heat of, 15
Naphthalene, alkylated, viscosity of, 38
—, as heat-transfer medium, 194
—, benzene from, 946
—, benzoic acid from, 950-952
—, by polymerization of cracking gas, 646
—, by pyrolysis of natural gas, 182, 183
—, 2,2′-dinaphthyl from, 208
—, effect on asphalts, 1208
—, estimation of, 1155
—, ethylated, lubricant from, 210
—, flotation agent from, 488
—, from acetylene, 720
—, from allyltoluene, 96
—, from butylbenzene, 74
—, from cyclohexane, 93
—, from 1,2-diethylcyclohexene, 94
—, from 2,6-dimethylanthracene, 96
—, from ethylbenzene, 96
—, from ethylene, 77, 186
—, from ethylhydrindene, 94
—, from isobutene, 85
—, from isooctylhydrindene, 94
—, from methane, 179, 180
—, from methylhexahydrohydrindene, 94
—, from methylhydrindene, 94
—, from methylisopropylhexahydrofluorene, 94
—, from propane, 61, 182
—, hydrogenated, in alcohol distillation, 327
—, hydrogenation of, 1154
—, in acetylene black, 244
—, in asphalt compositions, 1214
—, in crude oil, 179
—, in gasoline, 144
—, in kerosene, 36
—, in lubricating oil, 36
—, in motor fuel, 1039
—, in preparation of coloring matter, 215
—, labile isomers of, 179
—, lampblack from, 242
—, maleic acid from, 946
—, oxidation of, 260, 861, 945, 946, 950-953
—, phenols from, 953
—, phthalic anhydride from, 861, 946, 950
—, polymerization of, 260
—, quinones from, 953
—, reaction with acetyl chloride, 447
—, — *sec*-amyl alcohol, 409
—, — benzoic acid, 448
—, — chlorinated decane, 758
—, — chlorinated Kogasin, 1253, 1254
—, — chlorinated wax, 817
—, — cracked distillates, 212
—, — ethylene, 209, 210, 594
—, — propene, 593, 594, 596
—, — sodium, 957, 958
—, — sulphuric acid, 409
—, refining of, 745
Naphthalene carboxylic acids, from dihydronaphthalene, 958
—, from chloropyrenes, 956
Naphthalene sulphonic acid, catalyst, dehydration of alcohols, 411
—, —, hydration of olefins, 410
—, in wetting agents, 409, 1076
—, preparation of, 409
—, reaction with cyclohexanol, 410
—, — olefins, 314, 593
Naphthalene sulphonyl chloride, preparation of, 794
Naphthalic acid, from acenaphthene, 955

Naphthalic anhydride, from acenaphthene, 955
Naphthenates, antioxidants for lubricants, 933
Naphthenes, adsorption by carbon, 1149, 1150
—, — silica gel, 31
—, alkylated, viscosity of, 38
—, alkylation of, 594, 601, 602, 603
—, antiknock qualities of, 141, 1016
—, antioxidants for, 937
—, aromatics from, 196, 843
—, as gum fluxes, 915
—, asphaltenes from, 195, 196
—, by oxidation of petroleum hydrocarbons, 1043
—, carbenes from, 196
—, critical solution temperature, 42
—, definition of, 760
—, dehydrogenation of, 31, 33, 89, 92, 141, 179, 185, 1045
—, effect on acidity of lubricants, 932
—, — peroxide formation, 855
—, entropy of formation, 1284-1286
—, estimation of, 31, 1149, 1150, 1177
—, free energy of formation, 1284-1286
—, —, effect of temperature on, 1294
—, from ethyl alcohol, 342
—, from natural gas, 240
—, from olefins, 211, 636-639, 646
—, from petroleum, 40, 137
—, heat of formation, 1284-1286
—, identification of, 31
—, in gasoline, 28, 31-33
—, in kerosene distillates, 36
—, in petroleum, 13, 21, 33, 1149
—, in solid paraffins, 38
—, molal entropy of, 1284-1286
—, oxidation of, 843, 936
—, polymerized by silent electric discharge, 210
—, reaction with halogens, 760
—, *see also* Cycloparaffins
—, segregation of, 31
—, thermal stability of, 108, 137
Naphthenic acids, as source for petroleum, 20
—, as demulsifying agents, 1111, 1112
—, as extraction agent, 1073
—, as solvents, 1113
—, catalyst, sulphonation of paraffins, 1069
—, constitution of, 1103, 1110, 1111
—, determination of, 1104
—, extraction from petroleum, 1104-1109
—, glycol ethers from, 543
—, in alkali sludge, 1105
—, in cleaning agents, 1112
—, in crude petroleum, 10, 11, 1103
—, in detergents, 1112
—, in dispersing agents, 1112
—, in emulsifying agents, 1112
—, in fungicides, 1112, 1113
—, in insecticides, 1112, 1113
—, in lubricants, 1112
—, in petroleum distillates, 1103, 1104
—, in softening agents, 1112
—, in stabilization of gasoline, 1112
—, in wetting agents, 1112
—, naphthenic alcohols from, 1118
—, properties of, 1103, 1111
—, reaction with castor oil, 1113
—, — chlorosulphonic acid, 1118
—, — glycerol, 1112
—, — phenols, 1112, 1113
—, — silicic-acetic anhydride, 1116
—, — sulphuric acid ester, 1112
—, recovery of, 1107
—, reduction of, 1118
—, refining of, 1105, 1109, 1110
—, separation from sulphonic acids, 1065
—, silicon carboxylates from, 1116
—, sulphonation of, 1117, 1118
Naphthenic acid salts, as dispersing agents, 1117
—, as peptizing agents, 1116
—, effect of lead nitrate on, 1115
—, — manganese chloride on, 1115
—, in drying oils, 1115
—, in insulators, 1115
—, preparation of, 1115
Naphthenic acid salts, reaction with halogenated olefins, 1115
—, solubility of, 1115
Naphthenic acid soaps, as disinfectants, 1114
—, as emulsifying agents, 1114
—, detergent properties, 1113, 1114
—, effect of sodium carbonate on, 1113
—, — sodium hydroxide on, 1114
—, — sodium sulphate on, 1114
—, in brake fluids, 1114
—, in distillation of mineral oil, 1114
—, in insecticides, 1114
Naphthenic alcohols, as emulsifying agents, 1120
—, autoxidation of, 1118
—, chlorination of, 1120
—, esterification of, 1118
—, from naphthenic acids, 1118
—, in dispersing agents, 1120
—, in wetting agents, 1120
—, properties of, 1118, 1120
—, sulphonation of, 1120
Naphthenic bases, *see* Nitrogen bases
Naphthenic esters, as plasticizing agents, 1112, 1120
—, chlorinated, reaction with phenylates, 1120
Naphthenic oils, estimation by ultraviolet light, 1150
—, in lubricating oils, 41
α-Naphthol, antioxidant for decalin, 907
—, — gasoline, 916-918, 926
—, — transformer oil, 941
—, as blending agent, 1035
—, for stabilizing methyl chloride, 727
β-Naphthol, antioxidant for lubricants, 935
—, as blending agent, 1038
—, in insecticides, 790
—, reaction with acetylene, 715
α-Naphtholbenzein, antioxidant for gasoline, 917
Naphthols, color stabilizers, 926
—, antioxidants for Nujol, 940
—, — for tetralin, 906
—, reaction with glycol, 543
Naphthoquinone, preparation of, 950, 951
α-Naphthoquinone, condensation with butadiene, 175
—, — cracked distillates, 679
Naphthothioindigo, preparation of, 469
α-Naphthylamine, reaction with ethyl chloride, 808
Naphthylamines, antioxidants for gasoline, 918, 927
—, — Nujol, 940
—, — transformer oil, 941
—, as heat transfer agent, 420
—, for purification of alcohols, 408
Naphthyl phenyl ether, as heat-transfer medium, 861
β-Naphthyl phenyl ketone, from naphthalene-benzoic acid reaction, 448
2-Naphthyl-β-sulphoethylsulphone, preparation of, 618
Natural gas, acenaphthene from, 240
—, acetylene from, 168
—, analysis of, 1122
—, argon-nitrogen ratio in, 22
—, asphalt precipitation with, 1201
—, benzene in, 22
—, benzol from, 171
—, butanes in, 22
—, carbon black from, 220, 222, 228, 236, 237
—, carbon dioxide in, 22
—, classification of, 21
—, composition of, 22, 1121
—, ethane in, 22
—, extraction agent, 45
—, formaldehyde from, 862
—, gasoline from, 191
—, halogen derivatives from, 23
—, helium in, 22
—, hydrogen from, 220, 223, 228, 276, 278
—, hydrogen sulphide in, 22
—, in crude petroleum, 7
—, indene from, 155
—, methane in, 22
—, methyl alcohol from, 862
—, naphthenes from, 240

Natural gas, nitrobenzene from, 240
—, nitrogen in, 22
—, octane number of, 1033
—, oxidation of, 862, 880, 881
—, propane in, 22
—, pyrene from, 240
—, pyrolysis of, 155, 159, 160, 168, 171, 182, 183, 220-222, 225, 227, 228
—, reaction with carbon dioxide, 278
—, reaction with steam, 276
—, repressuring with, 9
—, solubility in hydrocarbons, 45
—, styrene from, 155
Natural resins, stabilizing carbon tetrachloride, 730
Neodymium oxide, catalyst, oxidation of aromatics, 942
—, —, — methyl alcohol, 878
Neon, effect on acetylene polymerization, 267
—, — ethylene oxide decomposition, 554
Neopentane, pyrolysis of, 67, 69
—, reaction with chlorine, 754
Neopentyl chloride, formation of, 754
—, properties of, 754, 755
Neoprene, definition of, 681
—, in synthetic rubber, 706
Neo-Spectra, definition of, 247
Neutral oils, from primary tars and chloroform, 729
Nickel, catalyst, alkylation of isobutane, 1301
—, —, allyl bromide-hydrogen bromide reaction, 316
—, —, carbonization of pinene, 88
—, —, chlorination of benzene, 779
—, —, combustion of natural gas, 225
—, —, dehydrogenation of borneol, 444
—, —, dehydrogenation of naphthenes, 31, 33, 89, 92, 179, 185
—, —, — paraffins, 149, 267
—, —, ethylation of amines, 346
—, —, ethylene-steam reaction, 271
—, —, hydration of ethylene, 291
—, —, hydrogenation of acetylene, 171, 1140
—, —, — butadiene, 699
—, —, — naphthalene, 1154
—, —, — olefin oxides, 586, 587
—, —, — olefins, 1146
—, —, — peanut oil, 1154
—, —, hydrogenation-polymerization of acetylene, 704
—, —, in cracking, 111, 114, 128, 129
—, —, in reforming, 280
—, —, methane-carbon dioxide reaction, 274
—, —, methane-steam reaction, 270-272, 276, 279, 1247
—, —, oxidation of aromatics, 942
—, —, — ethylene, 552, 553
—, —, — hydrocarbons, 1048
—, —, — hydrogen, 660
—, —, — methane, 224, 276, 869, 870
—, —, — paraffin oil, 907
—, —, — wax, 971, 1057
—, —, polymerization of acetylene, 704
—, —, — pinene, 645
—, —, pyrolysis of alcohols, 340, 348-350
—, —, — benzene, 95, 191
—, —, — halide mixture, 501
—, —, — halogenated ethers, 551
—, —, — olefins, 76
—, —, — of methane, 158, 180, 218
—, —, reaction of acetone and ammonia, 428
—, —, — carbon and hydrogen, 1278
—, —, — olefins and carbon monoxide, 626
—, —, reduction of acetone, 432
—, —, — carbon dioxide, 1241, 1242
—, —, — carbon monoxide, 1223-1225, 1228-1236, 1239-1244, 1248, 1249
—, —, — nitromethane, 1094
—, —, sulphuric acid absorption of olefins, 1135
—, electrodeposition of, 571
—, estimation of, 572
—, inhibitor, cyclization of paraffins, 138, 179
—, separation from cobalt, 572
—, stabilizer for ethylene oxide, 554
Nickel acetate, catalyst, oxidation of acetaldehyde, 885
—, —, pyrolysis of alcohol, 422
Nickel-alumina, catalyst, hydrogenation of toluene, 347
Nickel amines, as antiknocks, 1018
Nickel antimonides, catalysts, dehydrogenation of alcohols, 419
Nickel arsenides, catalysts, dehydrogenation of alcohols, 419
Nickel bismuthates, catalysts, dehydrogenation of alcohols, 419
Nickel boro-phosphate, catalyst, hydration of ethylene, 285
Nickel bromide, reaction with triethanolamine, 571
Nickel carbonate, catalyst, dehydrogenation of isopropanol, 420
—, —, methane-steam reaction, 278
—, —, oxidation of methane, 881
Nickel carbonyl, as antiknock, 1018
—, catalyst, reduction of carbon monoxide, 1240
Nickel chloride, catalyst, esterification of propene, 306
—, —, polymerization of olefins, 636, 665
—, —, pyrolysis of dichlorobutane, 510
—, —, pyrolysis of paraffins, 158
—, inhibitor, dechlorination of tetrachloroethane, 805
—, —, deposition of carbon, 191
Nickel chromate, catalyst, cyclization of aliphatic hydrocarbons, 74
—, —, pyrolysis of alcohols, 349
Nickel-chromium alloy, stabilizer for ethylene oxide, 554
Nickel-chromium oxide, catalyst, hydrogenation of glycerol, 547
Nickel compounds, catalyst, sulphation of ethylene, 323
Nickel cyanide, catalyst, sulphation of butenes, 391
—, —, sulphation of propene, 358
Nickel dimethyl, as antiknock, 1018
Nickel-free steel, for high pressure units, 134
Nickel halides, catalyst, dehydrogenation of hydrocarbons, 158
—, —, dichloroethane-hydrogen fluoride reaction, 747
—, —, olefin-carbon monoxide reaction, 625
Nickel hydroxide, catalyst, hydrocarbon-sulphur reaction, 467
—, —, methane-steam reaction, 278
Nickel iodide, reaction with triethanolamine, 571
Nickel naphthenate, as wetting agent, 1117
Nickel nitrate, in methane-steam reaction, 278
—, reaction with triethanolamine, 571
Nickel oxide, catalyst, cracking of petroleum, 111, 112, 137
—, —, dehydrogenation of alcohols, 422
—, —, — hydroaromatic hydrocarbons, 186
—, —, hydrogen-carbon monoxide reaction, 661
—, —, methane-steam reaction, 278, 279
—, —, oxidation of aromatics, 942
—, —, — methane, 881
—, —, — paraffin oil, 907
—, —, polymerization of olefins, 636, 637
—, —, pyrolysis of alcohol, 351
—, —, — methane, 54, 218, 227
—, —, — thiophene, 483
—, —, reaction of sulphur and hydrocarbons, 467
—, —, reforming of gasoline, 189
—, effect on ignition temperatures, 1000
Nickel oxide-alumina, catalyst, pyrolysis of ethylbenzene, 96
—, —, — ethylcyclohexane, 93
Nickel phosphides, catalysts, dehydrogenation of alcohols, 419
Nickel phthalate, benzaldehyde from, 952
—, benzoic acid from, 952
—, catalyst, decarboxylation of phthalic anhydride, 952
Nickel salts, catalyst, sulphation of propene, 358
—, inhibitors, condensation of isoolefins, 308
Nickel selenides, catalysts, dehydrogenation of alcohols, 419
Nickel soap, catalyst, oxidation of oils, 1044

Nickel sulphate, catalyst, acid absorption of olefins, 1142
—, —, ethylene oxide-glycol reaction, 558
—, reaction with triethanolamine, 571, 572
Nickel sulphide, catalyst, dehydrogenation of thiophane, 484
—, —, reaction of olefins and hydrogen sulphide, 462
Nickel tellurides, catalysts, dehydrogenation of alcohols, 419
Nicotine, stabilizer for gasoline, 917
Nicotine pyrogallate, antioxidant, 917
Nicotine sulphate, as insecticide, 1077, 1078
Nitrates, in motor fuel, 1039
Nitration, effect on ignition temperature, 1098
—, of acetic anhydride, 1090
—, of aromatic hydrocarbons, 31, 954, 1091, 1096, 1154
—, of chloroform, 729
—, of dimethylketone, 1090
—, of fuels, 1097
—, of gas oil, 1098, 1099
—, of olefins, 622
—, of paraffin hydrocarbons, 1087, 1088, 1090
—, of petrolatum, 1099
—, of waxes, 1092
Nitric acid, addition products with aldehydes, 851, 852
—, — ketones, 851, 852
—, catalyst, dehydration of tertiary alcohol, 410
—, —, hydration of olefins, 294-297, 410
—, —, isobutene oxide-alcohol reaction, 589
—, isolation of isoparaffins by, 31
—, oxidation of chlorinated ketones, 451
—, — naphtha, 881, 966
—, — paraffin wax, 974, 1054
—, — sapropels, 975
—, — wax distillates, 850
—, reaction with asphaltenes, 1191
—, — diethylene glycol, 546
—, — oil sludge, 935
—, — olefins, 621-623
Nitric oxides, catalysts, oxidation of acetylene, 903
—, —, — ethylene, 896
—, effect on aldehyde decomposition, 884
—, oxidation of paraffin hydrocarbons, 850, 851
—, reaction with paraffins, 1091
—, — methane, 281
Nitriles, amino acids from, 885
—, from acetylene, 719
—, from aldehydes, 886
—, from wax acids, 979
—, in co-polymerization of chloroprene, 681, 682
Nitrites, catalyst, polymerization of olefins, 672
Nitro-alcohols, from aldehydes, 888
Nitroanilines, antiknocks, 1017
—, antioxidants, 917
—, oxidation of benzyl alcohol, 851
Nitroarylamines, reaction with ethylene oxide, 560
Nitro aryl compounds, inhibitors, polymerization of chloroprene, 681
Nitro-asphalts, preparation of, 1191
Nitrobenzal bromide, oxidation of, 957
o-Nitrobenzaldehyde, for estimation of acetone, 424, 425
Nitrobenzaldehyde, from *p*-nitrobenzyl bromide, 957
Nitrobenzene, as refining agent, 41
—, catalyst, oxidation of naphtha, 876
—, estimation in oils, 1171, 1172
—, estimation of carbenes with, 1193
—, from natural gas, 240
—, in motor fuels, 1039
—, inhibitor, ethylene-sulphuric acid reaction, 322
—, —, polymerization of styrene, 805
—, solvent properties of, 1179
Nitrobenzoic acid, for oxidation of benzyl alcohol, 851
—, from nitrobenzal bromide, 957
p-Nitrobenzyl bromide, oxidation of, 957
Nitrobromobenzenes, for oxidation of benzyl alcohol, 851
Nitrobutanes, as lacquer solvents, 1098
Nitrocellulose, gels with alcohol, 330
—, plasticizers for, 541, 542
—, reduction of viscosity, 538
—, solvents for, 453, 558
Nitro compounds, in fuels, 1039, 1097, 1098
—, reaction with aldehydes, 888
Nitrocyclohexane, decomposition of, 1093
—, preparation of, 1091
—, reduction of, 1095
4-Nitro-*o*-cymene, preparation of, 382
4-Nitro-2,6-diisopropyltoluene, preparation of, 382
Nitroethane, reduction of, 1094
Nitroethyl nitrate, from ethylene, 622
Nitrogen, deasphalting agent, 45
—, determination of acetylene in, 701
—, diluent, benzene-ethylene oxide reaction, 563
—, —, carbon monoxide-methyl alcohol reaction, 1050
—, —, chlorination of hydrocarbons, 726, 813
—, —, in cracking operations, 115, 138
—, —, isomerization of propene oxide, 586
—, —, oxidation of hydrocarbons, 851, 860, 863
—, —, — olefins, 552, 553, 586, 893, 894
—, —, polymerization of acetylene, 267, 703, 704
—, —, — butadiene, 651
—, —, pyrolysis of methane, 219, 220
—, effect on carbon black yield, 237
—, — combustion, 1004
—, — ignition of carbon monoxide, 1001, 1002
—, — ignition temperature, 998
—, — inflammability limits, 984, 985
—, — Kogasin synthesis, 1235
—, — voltolization, 261
—, from oils, 131
—, inhibitor, ethylene oxide decomposition, 554
—, in natural gas, 22, 1121
—, separation from gas mixtures, 1133
Nitrogen bases, as antiknocks, 1017
—, as germicides, 842
—, as insecticides, 842
—, as oxidation inhibitors, 842
—, as pickling inhibitors, 841, 842
—, catalyst, hydration of olefins, 282
—, extraction from petroleum, 831, 832
—, from albuminous substances, 12
—, from anthracene oil, 839
—, from cottonseed meal, 840
—, from shale tar, 839, 840, 841
—, in distillates, 11
—, oxidation of, 839
—, phthalones from, 834, 836
—, reaction with bromine, 837
—, — formaldehyde, 836, 837
—, — phthalic anhydride, 836
—, resolution of, 837, 838, 839
—, structure of, 833-836
Nitrogen compounds, extractants for asphalts, 1202
—, in crude oil, 10, 17
Nitrogen content, of petroleum, 831, 832
Nitrogen dioxide, catalyst, oxidation of ethane, 850
—, nitration of benzene, 1091
—, oxidation of paraffin wax, 974, 975
—, refining of naphthenic acids, 1109
Nitrogen oxides, catalyst, carbon monoxide-alcohol reaction, 1050
—, —, for aquolization, 132
—, —, oxidation of anthracene, 953
—, —, — ethane, 872
—, —, — hydrocarbons, 850
—, —, — methane, 870, 881, 882
—, desulphurizing agents, 490
—, oxidation of paraffins with, 892
—, — olefins with, 490, 896
—, reaction with stilbene, 621
—, reduction by hydrogen, 276
—, removal of phenols with, 135
Nitrogen pentoxide, reaction with acetic anhydride, 1090
—, — olefins, 621
Nitrogen peroxide, reaction with olefins, 620
Nitrogen tetroxide, from nitrolic acids, 1094
—, reaction with cyclohexane, 1091
—, — ethylene, 620

Nitrogen tetroxide, reaction with hexane, 1090
—, — pentene, 620, 621
—, — tetramethylethylene, 621
—, — trimethylethylene, 621
Nitrogen trichloride, reaction with ketene, 440
Nitrogen trioxide, reaction with olefins, 620, 696, 697
Nitrogenous substances, effect on color stability, 925
Nitro-glycols, from aldehydes, 888
2-Nitrohexane, preparation of, 1090
—, reduction of, 1094
Nitrohydrin, from olefins, 622
Nitrolic acids, aniline diazotized by, 1094
—, decomposition of, 1094
—, from nitroparaffins, 1093
—, reaction with sulphuric acid, 1094
—, reduction of, 1094
Nitromethane, carbon remover, 1098
—, chloropicrin from, 1096
—, reaction with ammonium hydroxide, 1096
—, — sulphuric acid, 1096
—, reduction of, 1094
—, solvent properties of, 1179
—, thermal decomposition of, 1096
—, Raman effect of, 1092
Nitronaphthalene, use as wood preservative, 790
Nitro-nitrate, from tetramethylethylene, 621, 622
Nitroparaffins, as refining agents, 1098
—, nitrolic acids from, 1093
—, pseudonitroles from, 1093
—, reaction with aldehydes, 1095
—, — alkylmagnesium iodides, 1096
—, — carbon disulphide, 1096
—, — diketones, 1096
—, reduction of, 1094, 1095
p-Nitrophenylazopyrogallol, antioxidant, 916
Nitropropane, reaction with hydrochloric acid, 1096
—, toxicity of, 1097
Nitropropanes, as lacquer solvents, 1098
Nitro radicals, as gum inhibitors, 914
Nitrosate, from ethylene, 621
—, from pentene, 620, 621
—, from tetramethylethylene, 621
Nitrosite, from allene, 696, 697
—, from butene-1, 620
—, from dimethylbutadiene, 697
—, from 2-methylbutene-2, 620
—, from 2-methylpropene, 620
—, from trimethylethylene, 621
Nitrosochlorides, from olefins, 619
Nitrosonaphthols, antioxidants, 917
Nitrosonaphthylamines, antioxidants, 917
Nitrosophenols, antioxidants, 917
Nitrosopropylhydroxybenzenes, antioxidants, 917
Nitrosyl chloride, catalyst, cracking of petroleum, 112
—, for reactivation of aluminum chloride, 198
—, reaction with butane, 1101
—, — *n*-hexane, 1101
—, — olefins, 619
—, — paraffins, 1102
—, — toluene, 794
Nitrotoluene, from crude oil, 35
Nitrous oxide, catalyst, decomposition of acetaldehyde, 884
—, effect on blood, 1260
—, — erythrocytes, 1261
—, — leucocytosis, 1268
—, from nitrolic acids, 1094
—, in oxidation of acetaldehyde, 851
—, — carbon disulphide, 851
—, — ethylene, 851, 896
—, — methyl alcohol, 851
—, — phosphine, 851
Nomogram, definition of, 1170
Nonane, from carbon monoxide and hydrogen, 1243
—, in petroleum, 32
—, in shale oil, 32
—, pyrolysis of, 72
Nonaphthene, in crude oil, 34
Nonene, from carbon monoxide and hydrogen, 1243
—, in gasoline, 144
—, in shale oil, 32
—, polysulphone from, 618
—, reaction with benzene, 591
—, reaction with sulphur, 618
Nonenes, from propene, 639
—, from tertiary alcohols, 411
3-Nonyn-1-ol, preparation of, 565
Nujol, antioxidants for, 940

O

Octacosene, from isobutene, 643
Octadecane, from carbon monoxide and hydrogen, 1245
—, pyrolysis of, 73
—, reaction with aluminum chloride, 201
1,12-Octadecanediol, octadecenol from, 548
Octadecene, in kerosene, 145
Octadecenol, from 1,12-octadecanediol, 548
Octahydronaphthalene, reaction with mercuric acetate, 628
Octanaphthenes, in petroleum, 33
Octane, chlorination of, 756
—, cracking of, 100
—, dehydrogenation of, 101
—, ignition temperature of, 991
—, inflammability limits of, 980, 981, 985, 986
n-Octane, energy of activation of, 72
—, ethylbenzene from, 73
—, free energy of formation, 1225
—, from carbon monoxide and hydrogen, 1243
—, from petroleum, 32
—, from *n*-tetradecane, 1297
—, in gasoline, 144
—, isomerization of, 70
—, isooctane from, 199
—, pyrolysis of, 72
—, reaction with aluminum chloride, 199
—, — molybdenum sulphide, 72
—, *o*-xylene from, 73, 74
Octane number, comparison with blending octane number, 1026
—, definition of, 1025
—, factors affecting, 1027, 1028, 1030-1033
—, function of cracking temperature, 106
—, increase on cracking, 105
—, in knock rating, 1025-1027
—, of alcohols, 1028
—, of aromatics, 1028
—, of cycloolefins, 1028
—, of cycloparaffins, 1028
—, of olefins, 1028
—, of paraffins, 1028
—, significance of, 142
—, *see also* Knock rating
Octanol-2, reaction with phosphoric acid, 400
Octene, action of silent discharge on, 258
—, chlorohydrin from, 522
—, from isobutene, 643
—, from nonane, 72
—, in cracked gasoline, 144
—, inhibitor, oxidation of aldehydes, 899
—, oxidation of, 899
—, reaction with aniline, 615
—, — benzene, 591
2-Octene, from carbon monoxide and hydrogen, 1243
—, 2-methyl-1,3-octanediol from, 624
Octenes, from dehydration of alcohols, 400
Octylacetylene, preparation of, 722
Octyl alcohol, from butyraldehyde, 889
—, by pyrolysis of alcohols, 339, 340
sec-Octyl alcohols, plasticizers, for cellulose nitrate, 409
—, solubility in water, 404
Octyl pyrogallol, antioxidant, for gasoline, 916
1-Octyne, preparation of, 722
3-Octyn-1-ol, preparation of, 565
Oenanthaldehyde, as antiknock, 1017
Oil absorption, of carbon black, 246
Oil residues, oxidation to asphalts, 1043

Oils, by oxidation of petrolatum, 1056
—, effect of refining on stability of, 940
—, electrical cracking of, 131
—, extraction from asphalts, 1200
—, flash point, determination of, 1170, 1171
—, from acetylene polymerization, 703
—, from cellulosic material, 21
—, from chlorinated paraffin wax, 758
—, from petrolenes, 1202
—, sulphates reduced by, 48
—, treatment with oleum, 1069
—, white, antioxidants for, 936, 937
Oil-shales, porphyrins in, 12, 19, 20
Oil sludge, reaction with nitric acid, 935
Oil-still gas, hydrogen from, 223
Oil wells, acidation of, 9
Olefin halides, decomposition of, 807
—, dehalogenation of, 146
—, peroxides in formation of, 315
—, reaction with aromatics, 592, 593
Olefinic acids, chlorohydrins from, 627
—, lactones from, 627
—, reaction with hypochlorous esters, 627
Olefin oxides, by oxidation, 551-553
—, from chlorohydrins, 524, 550
—, glycol ethers from, 548
Olefins, acetylene from, 255
—, acids from, 625
—, action of silent discharge on, 258, 259
—, adsorption by carbon, 328
—, alcohols from, 161, 359, 893
—, aldehydes from, 553
—, antiknock qualities of, 141, 1016
—, aromatics from, 190, 211
—, bromination of, 146, 1142, 1143, 1152
—, butadiene from, 171
—, by oxidation of paraffins, 843, 876, 892
—, by polymerization of acetylene, 703
—, carbon black from, 237
—, catalysts, chlorination of propane, 750
—, chlorination of, 493
—, classification of, 308, 385, 386
—, dichlorodialkyl ethers from, 628
—, dimerization of, 101, 102
—, entropy of, 1282-1284, 1290, 1291
—, esterification of, 307, 308, 376
—, estimation of, 1124, 1141-1146, 1150-1154
—, ethers from, 331
—, ethylene glycol dinitrate from, 622
—, factors in formation of, 148
—, free energy of formation, 1282-1284, 1294, 1295
—, from alcohols, 313, 337, 347, 420
—, from aliphatic hydrocarbons, 148, 154-160
—, from alkyl halides, 804-806
—, from aromatics, 95, 96, 148
—, from butanes, 61-67, 152, 153, 160
—, from carbon monoxide and hydrogen, 1235, 1242, 1243
—, from cracked gases, 139, 140
—, from cycloparaffins, 89-95, 148
—, from ethylene, 636, 637, 638, 639
—, from heptanes, 71, 72, 153, 154
—, from hexanes, 69-71, 153, 154
—, from Kogasin, 1252
—, from methane, 257
—, from nonane, 72
—, from octane, 70, 72
—, from pentanes, 67-69, 153
—, from toluene, 260
—, glycols from, 532, 547, 624
—, halogenation of, 1152
—, heat of formation, 1282-1284
—, hydrogenation of, 670, 671, 1154
—, hydroxylation of, 532, 534, 535, 895
—, in cracked distillates, 141-146
—, in gasoline, 136, 143, 155
—, —, estimation, 1149, 1150
—, —, oxidation of, 895, 1045
—, —, polymerization of, 929
—, in oxidized asphalt, 1206
—, in petroleum, 17
—, naphthenes from, 211
—, 2-nitroethyl nitrate from, 622
Olefins, nitrohydrin from, 622
—, nitrosates from, 620
—, nitrosites from, 620, 621
—, nitrosochlorides from, 619
—, octane numbers of, 1028
—, oxidation of, 532, 553, 892-894, 896, 898, 900, 907, 923
—, ozonolysis of, 901, 902
—, polycarboxylic acids from, 629
—, polymerization, by heat, 76, 107, 149, 160, 631, 646, 655-661, 671, 672, 1041, 1042, 1252
—, —, by aluminum chloride, 202, 209, 215, 255, 635, 671
—, —, by metals, 665
—, —, by phosphoric acid, 390, 634, 646, 662-664
—, —, by silent discharge, 210, 256
—, —, by sulphuric acid, 255, 385, 395, 400, 401, 411, 649
—, polymerized, depolymerization of, 101
—, purification of, 161, 214
—, reaction with acid halides, 609-614
—, — acid sludge, 669
—, — aldehydes, 623-625
—, — alkali hydroxides, 629
—, — alkyl hypochlorites, 626
—, — aluminum chloride, 209, 216
—, — amines, 614, 615
—, — ammonia, 281, 614, 615
—, — aromatics, 209, 591-598
—, — carbon monoxide, 625, 626
—, — cellulose, 629
—, — chloroethers, 613
—, — cholorsulphonic acid, 609
—, — ethylene glycol hypochlorite, 628
—, — halogenated esters, 613, 614
—, — halogens, 491
—, — hydrogen halides, 298, 301, 307, 311
—, — hydrogen peroxide, 547
—, — hydrogen sulphide, 462, 463
—, — hydroxy aromatic acids, 607
—, — inorganic salts, 628
—, — maleic anhydride, 629
—, — mercury salts, 628, 1149-1151
—, — monocarboxylic acids, 308, 314
—, — naphtha, 592
—, — naphthenes, 209, 211
—, — nitric acid, 622
—, — nitrogen oxides, 620, 621
—, — nitrosyl chloride, 619
—, — paraffins, 200, 598, 599, 601
—, — phenols, 383, 412, 603-607
—, — phosgene, 609, 611
—, — selenium dioxide, 895
—, — sodium cyanide, 305
—, — steam, 270
—, — sulphites, 616
—, — sulphonic acids, 314, 393
—, — sulphur, 455, 456, 468
—, — sulphur chloride, 618
—, — sulphur dioxide, 616
—, — sulphuric acid, 161, 298, 359, 391-393, 1083, 1142
—, — sulphurous acid, 616
—, — thiocyanogen, 629, 1152, 1153
—, removal from cracking gas, 324, 358
—, — from gasoline, 927
—, — of sulphur compounds from, 398
—, resins from, 215, 618, 625
—, *see also* Unsaturates
—, separation, from acetylene, 161
—, —, from butadiene, 161
—, —, from gas mixtures, 161-164, 1135
—, —, from hydrogen, 161, 165
—, —, from isobutene, 210
—, —, from naphthenes, 31, 1155
—, —, from paraffins, 31, 161-163, 190, 1155
—, —, with sulphuric acid, 389, 390
—, sulphonation of, 669, 1081, 1082
—, sulphones from, 616-618
—, sulphonic acids from, 616
—, thermal stability of, 72, 76, 101, 631, 632, 892
—, voltolization of, 261
ter-Olefins, separation, from amylenes, 310

Oleic acid, in cleaning agents, 746
—, in fungicides, 569
—, oleone from, 446
—, reaction with benzene, 815
—, — dichloroethane, 815
—, — hydrogen fluoride, 307
—, — isethionic acid, 1082
—, — ozone, 902
—, voltolization of, 261
Oleic soap, detergent properties of, 1113
Oleone, from oleic acid, 446
Oleo-resins, source for petroleum formation, 19
Oleum, in treatment of distillates, 1069
—, reaction with aliphatic acids and acetic anhydride, 1086
—, — ethylene, 1082
Oleyl alcohol, oleyl sulphate from, 1084
—, reaction with ethylene oxide, 558
Oleyl ethylenediamine, use as detergent, 809
Oleyl halides, glycol ethers from, 543
Oleyl sulphate, from oleyl alcohol, 1084
Osmium chloride, catalyst, polymerization of isobutene, 204
Osmium octafluoride, catalyst, polymerization of isobutene, 642
Osmium tetroxide, activator, for hydrogen peroxide, 547, 895
—, catalyst, oxidation of cyclohexene, 852
—, —, oxidation of mercaptans, 480
—, —, oxidation of olefins, 532
Osmosis, in separation of sulphonates, 1073
Oxalic acid, catalyst, hydration of olefins, 297, 410
—, —, dehydration of tertiary alcohols, 410
—, from acetylene, 904
—, from dioxane, 580
—, from ethylene, 622
—, from isopropyl alcohol, 371
—, reaction with 3-hydroxy-3,4-di-*ter*-butyl-1-butene, 679
Oxamic acids, inhibitors, gum formation, 915
Oxidation, effect, on antiknock properties, 864
—, electrolytic, of hydrocarbons, 853, 854, 953, 954
—, hydrogen estimation by, 1128
—, in refining processes, 1041, 1042
—, liquid phase, of hydrocarbons, 864, 865, 962, 965
—, mechanism of, 844-849
—, of acenaphthene, 946, 955
—, of acetaldehyde, 851, 885, 889
—, of acetone, 853
—, of acetophenone, 853
—, of acetylene, 849, 850
—, of alcohols, 399, 420, 423, 844, 849, 877-880, 931
—, of aldehydes, 885, 889
—, of aliphatic acids, 852
—, of ammonia-methane mixture, 871
—, of anthracene, 952-954
—, of aromatics, 942-961, 1155
—, of asphaltenes, 1191
—, of asphalts, 1202-1205
—, of benzaldehyde, 957
—, of benzene, 850, 855, 942, 944, 945, 953
—, of benzoin, 953
—, of benzyl alcohol, 851
—, of benzyl chloride, 957
—, of butane, 852, 859, 863, 874
—, of butyl alcohol, 880
—, of carbon disulphide, 851
—, of carbon monoxide, 850
—, of ceresins, 975
—, of chlorobenzene, 944
—, of cracking gas, 881
—, of crude oils, 938, 1190
—, of cyclohexane, 854, 855, 874, 876
—, of cyclohexene, 852
—, of cyclopentane, 876
—, of cylinder oil, 1043
—, of diethyl ether, 335
—, of diethyl trisulphide, 481
—, of diolefins, 666
—, of diphenylmethane, 943, 957
—, of ethane, 846-848, 850, 856-858, 871-873, 1129, 1130
—, of ethyl alcohol, 844, 872, 879, 880
—, of ethylbenzene, 942, 943
—, of ethylene, 844, 847-849, 851, 896
Oxidation, of fluorene, 954, 955
—, of fluoroform, 737
—, of *p*-fluorotoluene, 954
—, of foots oil, 972
—, of furfuraldehyde, 945
—, of gas oil, 863
—, of gasoline, 855, 861, 864, 908, 1046
—, of glycols, 536, 546, 548, 549
—, of heptane, 843, 850, 851, 859, 873-875, 1015, 1016
—, of 3-heptene, 875
—, of hexachloropyrene, 956
—, of hexadecene-1, 548
—, of hexane, 850, 851
—, of hydroformed solvents, 1054
—, of hydrogen sulphide, 460, 461
—, of kerosene, 859, 860, 946, 965, 966, 1047
—, of Kogasin, 1255
—, of lubricating oil, 41, 855, 931-935, 937, 938, 1055
—, of mercaptans, 470, 471, 480, 1066, 1158
—, of mesitylene, 954
—, of methane, 845-849, 857, 858, 866-871, 880-883, 995, 1246
—, of methyl alcohol, 851, 877-879
—, of 2-methylbenzanthrone, 957
—, of methyl chloride, 849
—, of methylcyclohexane, 843
—, of methylene chloride, 849
—, of naphtha, 875, 876, 881, 966
—, of naphthalene, 861, 945, 946, 950-953
—, of naphthenes, 843, 936
—, of natural gas, 862, 880, 881
—, of nitrobenzal bromide, 957
—, of *p*-nitrobenzyl bromide, 957
—, of olefins, 532, 629, 892-902
—, of paraffin oils, 876
—, of paraffin wax, 843, 846, 856, 860, 865, 962, 970-979, 1054, 1057, 1086, 1255
—, of pentane, 852, 859, 860, 864, 865, 994, 995
—, of petrolatum, 972, 1056
—, of petroleum distillates, 962-966
—, of petroleum ether, 853-854
—, of phenols, 849
—, of phosphine, 851
—, of pinacol, 536
—, of pinene, 855
—, of polyhydric alcohols, 548
—, of propane, 848, 850, 851, 858, 859, 862, 863, 872-874
—, of residuum oils, 1043
—, of rubrene, 848, 849
—, of sapropels, 975
—, of slop wax, 972
—, of sodium hydrosulphide, 465
—, of solar oil, 940, 964, 965
—, of sulphurated paraffins, 1083
—, of tetrachloropyrene, 956
—, of thioethers, 479, 480
—, of thiosulphates, 1083
—, of toluene, 843, 942-944, 947-950, 953, 954
—, of transformer oil, 938-940, 963
—, of triethylmethane, 876
—, of triphenylmethane, 943, 957
—, of wax distillates, 850
—, of white oils, 856, 936
—, photochemical, of hydrocarbons, 966
—, vapor phase, of hydrocarbons, 862-864, 965, 966
Oxidation number, definition of, 856
—, of lubricants, 931
Oxidized asphalts, manufacture of, 1205
Oxidized paraffins, as demulsifying agents, 1061
—, in flotation agents, 1060
Oxonium compounds, from asphaltenes, 1191
Oxygen, absorption rate by oils, 931
—, effect on decomposition of aldehydes, 884
—, — halogenation reactions, 684, 700, 750, 769, 778
—, — hydrocarbon pyrolysis, 153, 160
—, — polymerization of olefins, 636, 641, 650, 661, 1041, 1042
—, — reaction of olefins and hydrogen halides, 315, 316, 686
—, estimation in gases, 1124, 1259

Oxygen, in gum from gasoline, 911
—, in hydroxylation of olefins, 534
—, in preparation of sulphones, 696
—, in refining petroleum distillates, 671, 1043, 1044
Ozone, as desulphurizing agent, 489, 490, 1044, 1045
—, catalyst, oxidation of paraffins, 852
—, —, reaction of propene and sulphur dioxide, 617
—, effect on ignition temperatures, 998
—, for phenol removal, 135
—, reaction with acetylenes, 904
—, — aldehydes, 887
—, — gasoline, 1044
—, — mesityl oxide, 901
—, — olefins, 901, 902
—, — organic acids, 902, 904
—, — paraffin wax, 974

P

Paint driers, *see* Driers
Paint remover, preparation of, 790
Paints, asphalts in, 1192
—, cellulose esters in, 1115
—, naphthenates in, 1115
Paint thinners, by oxidation of hydrocarbons, 865
Paint vehicles, by oxidation of oils, 1055
Palladium, catalyst, dehydrogenation of alcohols, 1051
—, —, — cycloparaffins, 90, 92, 94
—, —, — naphthenes, 31
—, —, — vinylcyclohexane, 93
—, —, ethers from acetals, 715
—, —, hydrogenation of unsaturates, 699, 1153, 1154
—, —, oxidation of aromatics, 942
—, —, — hydrogen, 1127, 1128
—, —, — methane, 869
—, —, polymerization of olefins, 665
—, —, reaction of acetylene and amines, 719
—, —, — methane and steam, 279
—, —, reduction of carbon monoxide, 1223, 1241
—, effect on ignition temperatures, 1000
Palladium alloys, catalysts, in cracking, 113
Palmitates, catalysts, oxidation of paraffin wax, 971
Palmitic acid, in drying agents, 1115
—, molal entropy, 1292, 1293
Paneth effect, 51
Parachor, determination of, 1180, 1181
Paraffin acids, reaction with pentaerythritol, 1055
Paraffin hydrates, formation of, 27
Paraffin oil, asphalts from, 1199
—, chlorinated, lubricants from, 214
—, cracking of, 103
—, estimation of, 1150
—, from benzine, 155
—, from resins, 1189
—, oxidation of, 876, 906
Paraffins, adsorption by carbon, 1149, 1150
—, — silica gel, 31
—, antiknock qualities of, 141
—, aromatics from, 186, 187
—, autoxidation of, 905
—, boiling points, 14, 15
—, characterization factor of, 1307
—, combustion of, 999, 1015
—, cracking of, 141
—, dehydrogenation of, 52
—, —, free energy change, 1284, 1298
—, density of, 1134, 1135
—, effect of lead tetraethyl on, 1019
—, effect on viscosity of crystal oil, 15
—, entropy of formation, 1279-1281
—, estimation of, 1149, 1150, 1177, 1199
—, extraction agents for isopropyl alcohol, 364
—, fatty acids from, 1088
—, free energy of formation, 1279-1281
—, —, effect of temperature on, 1294, 1295
—, from carbon monoxide and hydrogen, 1242, 1243, 1245
—, from cycloparaffins, 205, 206
—, from olefins, 636-639, 646
Paraffins, heat of formation, 1279-1281
—, in crude oil, 13, 1149
—, in gasoline, 28, 31, 32
—, isomerization of, 202
—, lubricants from, 813, 814
—, melting points of, 14
—, molal entropy, 1279-1281
—, —, effect of structure on, 1288
—, octane numbers of, 1028
—, olefins from, 148, 843
—, —, free energy change, 1284
—, oxidation of, 843, 1088
—, polymerization of, 210
—, pyrolysis of, 61, 71, 73, 154, 892
—, reaction with aluminum chloride, 198-202
—, — antimony chloride, 1102
—, — bromine, 759
—, — carbon monoxide, 1099
—, — chlorine, 740, 813
—, — chlorosulphonic acid, 1102
—, — chromyl chloride, 1102
—, — nitric acid, 1087 1090
—, — olefins, 598, 599, 601
—, — sulphur, 1102
—, — sulphur monochloride, 1102
—, removal, by distillation, 162, 163
—, —, with chlorosulphonic acid, 32
—, —, with sulphuric acid, 31
—, stability during cracking, 101, 108
—, thermal clevage of, 99
—, voltolization of, 261
Paraffin wax, acids from, 843, 856, 865, 970, 971, 1255
—, alcohols from, 865, 971, 973
—, aldehydes from, 865, 971
—, chlorination of, 757
—, cracking of, 138, 212
—, critical solution temperature, 42
—, esters from, 971, 972
—, estimation of, 1155, 1156, 1164
—, fluorination of, 759
—, from carbon monoxide and hydrogen, 1250
—, from crudes, 13, 38-40
—, from pyroschists, 145
—, hydrogenation of, 179
—, in candles, 543, 1255
—, in plasticizing agents, 1054
—, in polishing compositions, 1079
—, ketones from, 971
—, lactic acid from, 971
—, lactones from, 971
—, lubricating oils from, 212
—, oxidation of, 843, 856, 860, 865, 962, 970-979, 1054, 1086, 1255
—, —, mechanism, 972, 973
—, pour point depressant from, 215
—, pyrolysis of, 179
—, reaction with sulphur dioxide and chlorine, 756
—, refined, solubility of, 38
—, separation, from Kogasin, 1245
—, sulphates from, 1086
Paraflow, as dewaxing agent, 758
—, as pour point depressant, 758, 817
Paraformaldehyde, from formaldehyde, 877
—, reaction with ethylene glycol, 582
Paraldehyde, structure of, 886
Parasiticide, from carbon tetrachloride, 733
Peanut oil, hydrogenation of, 1154
Peat, carbon from, 227
—, chlorination of, 227
—, in storing acetylene, 171
Peat tar, ethylene from, 155
—, motor fuel from, 135
Peneration, of asphalts, definition of, 1208
Penetration agents, preparation of, 558, 569
Penetration-temperature relation, of asphalts, 1211
Penetrol, in insecticides, 1078
Pentabromobenzene, from benzene, 790, 791
Pentabromotoluene, preparation of, 775
Pentachlorobiphenyl, in dielectrics, 789
Pentachlorobutane, preparation of, 811
—, resins from, 217
Pentachloroethane, as solvent, 495
—, reaction with sulphuric acid, 830
6,9-Pentadecadiyne, reaction with ozone, 904

Pentadecenes, from propene, 639
Pentadiene, from acetylene, 75
1,4-Pentadiene, from *n*-pentane, free energy change, 1284
—, molal entropy, 1291
Pentaerythritol, reaction with fatty acids, 1055
Pentafluorochloroethane, preparation of, 735
Pentamethylbenzene, molal entropy, 1290
Pentamethylene, *see* Cyclopentane
Pentamethylene alcohols, esterification, 1118, 1119
Pentamethylethyl bromide, hexamethylethane from, 759
Pentamethylpentanol, *see* Methyl-di-*ter*-butylcarbinol
Pentane, acids from, 859
—, alcohols from, 859, 864
—, as anesthetic, 1256
—, as motor fuel, 1040
—, combustion of, 1011, 1012
—, decolorizing agent for resins, 216
—, estimation of, 1134
—, explosive characteristics of, 1011, 1012
—, from amylene, 630
—, from carbon monoxide and hydrogen, 1242, 1243
—, from ethylene and propane, 601
—, from *n*-hexane, 198
—, heat of combustion, 15
—, ignition, 1009, 1010
—, ignition temperature of, 987, 988, 992, 995, 1000
—, inflammability limits of, 985, 986
—, in gasoline, 144
—, in petroleum gases, 21
—, isomerization of, 201, 445
—, lower paraffins from, 68
—, 3-methylbutane from, 445
—, olefins from, 68, 153
—, oxidation of, 852, 859, 860, 864, 865
—, —, mechanism, 994, 995
—, 1, 4-pentadiene from, free energy change, 1284
—, pyrolysis of, 67, 68, 149, 153
—, reaction with acetyl chloride, 444, 1099
—, — aluminum chloride, 201
—, — ammonia, 810
—, — chlorine, 753, 754
—, — nitric oxide, 1091
—, — phosgene, 445
—, solvent for ketene, 435
—, thermodynamic relations of, 15, 1333, 1334, 1338, 1339
1.2-Pentanediol, oxidation of, 549
Pentanol, from ethyl alcohol, 347
—, *see also* Amyl alcohol
2-Pentanol, from cracked gasoline, 388
—, from pentenes, 318, 387, 404
—, from propene oxide, 586
3-Pentanol, from pentenes, 318, 387, 404
—, from propene oxide, 586
Pentasol, in rubber cement, 374
2-Pentene, aromatics from, 87
—, *sec*-diamyl sulphate from, 309
—, oils from, 204
—, polymerization of, 204, 210, 643
—, propene from, 87
1-Pentene dichloride, *see* 1-Amylene dichloride
1-Pentene oxide, reaction with dimethylamine, 589
Pentenes, butenes from, 86
—, effect of tetraethyl lead on, 1021
—, ethane from, 86
—, ethylene from, 86
—, from carbon monoxide and hydrogen, 1243
—, from ethyl alcohol, 173
—, from ethylene, 639
—, from isopentane, 69
—, from kerosene, 144
—, from nonane, 72
—, from pentane, 68
—, from propene, 79, 641
—, from sapropelite tar, 144
—, in gasoline, 144
—, isomerization of, 86
—, methane from, 86, 87
—, nitrosate from, 620, 621
—, pentanol from, 387
—, polysulphones from, 618
Pentenes, pyrolysis of, 85-87, 184
—, reaction with acetic acid, 313
—, — benzene, 591
—, — formic acid, 312
—, — hydrogen bromide, 317, 318
—, — hydrogen chloride, 310
—, — nitrogen tetroxide, 620, 621
—, — sulphur dioxide, 618
—, — sulphuric acid, 308, 318, 387, 388, 391
Pentyl chloride, *see* Amyl chloride
1-Pentyne, from 1,2-dibromopentane, 514
—, from 1-pentene, 146
3-Pentyn-1-ol, preparation of, 565
Peptizing agents, benzol as, 1196
—, carbon disulphide as, 1196
—, naphthenic acid salts as, 1116
—, pyridine as, 1196
Peracetic acid, from acetaldehyde, 899
—, oxidizing agent for olefins, 490, 899, 900
Peracids, in gasoline, 909
Perbenzoic acid, from benzaldehyde, 899
—, oxidizing agent for octene, 899
—, reaction with asphaltenes, 1191
—, — 1,3-cyclohexadiene, 589
Perchloric acid, catalyst, isomerization of 1-butene, 82
Perchloroethylene, chlorination of, 742
Perfumes, from aldehydes, 881
—, from diolefins, 676
—, from quinones, 690
Perhalates, oxidizing agent for oils, 1054
Permanganates, refining agent for gasoline, 929
Permutites, catalysts, isomerization of propene oxide, 586
Peroxide number, definition of, 924
—, of autoxidized olefins, 907
Peroxides, effect on antiknock value, 924
—, — gum formation, 908, 921, 924
—, — reaction of olefins and hydrogen halides, 315-317, **356, 716, 723**
—, estimation of, 381
—, from acetylenes, 924
—, — acetone, 431
—, — aliphatics, 845
—, — aromatics, 922
—, — butyl ether, 336
—, — cyclohexane, 854, 855, 874
—, — diolefins, 931
—, — ethyl ether, 335-337
—, — hexane, 1014
—, — isopropyl ether, 336, 381
—, — mineral oil, 856
—, — propane, 873
—, in gasoline, 908, 922
—, reaction with hydrogen halides, 317
—, — silver oxide, 381
—, removal from gasoline, 923
—, use in motor fuel, 1039
Persulphates, desulphurizing agents, 490
Persulphuric acid, reaction with olefins, 309, 490, 532
Perylene, as antioxidant, 918
—, from dinaphthyl, 208
Petrolatum, coal sprayed with, 41
—, cracking of, 213
—, extraction with acetone, 37
—, — butane, 972
—, — propane, 972
—, in grease, 1079
—, oils from, 1056
—, oxidation of, 972, 1056
—, pour point depressant from, 215
—, reaction with carbon tetrachloride, 732
—, — nitric acid, 1099
—, resin from, 732
—, sulphonic acids from, 1069
Petrolenes, in asphalts, 1198
—, oils from, 1202
—, resins from, 1202
Petroleum acids, asphalts from, 1112
Petroleum aldehydes, in synthetic plastics, 890
Petroleum bases, as pickling inhibitors, 841
Petroleum-coal distillate, chlorination of, 781
Petroleum coke, *see* Coke

Petroleum distillates, cracking of, 197
—, in insecticides, 1112
—, naphthenic acids in, 1103
—, reaction with sulphur trioxide, 1069
—, resins from, 814, 815
—, solvent extraction, 41
—, specific heats of, 15
—, sulphonic acids from, 1069
—, synonyms for, 11
Petroleum ether, extraction agent for *sec*-butyl alcohol, 407
—, — isopropyl alcohol, 365
—, oxidation of, 853, 854
Petrozcene, extraction with benzine, 1189
Pharmaceuticals, from diolefins, 676
β-Phellandrene, reaction with nitrous acid, 620
β-Phellandrene nitrosite, preparation of, 620
Phenanthrene, as antioxidant, 916, 918, 927
—, from acetylene, 720
—, from cracking gas, 646
—, from natural gas, 183
—, from propane, 61, 182
—, in acetylene black, 244
—, in petroleum coke, 145
—, pyrolysis of, 37
—, reaction with aluminium chloride, 208
—, — isobutyl chloride, 827
Phenethyl alcohol, *see* Phenylethyl alcohol
Phenetole, extraction agent for alcohol, 360
—, — ketene, 437
Phenol, acetylation of, 438
—, adsorption by carbon black, 252
—, alkylation of, 384
—, as antioxidant, 907, 915
—, diphenyl ether from, 788, 789
—, extraction agent for asphalts, 1202
—, — ethyl alcohol, 360
—, — petroleum oils, 42, 134, 746, 1205
—, from benzene, 260, 942
—, in lubricating oils, 42
—, phenylphenol from, 785
—, preparation of, 782-784, 943
—, reaction with acetylene, 715
—, — *ter*-butyl alcohol, 412
—, — *ter*-butyl chloride, 418, 818
—, — chlorobenzene, 784, 785, 788, 789
—, — *sec*-hexanol, 403
—, — isopropyl alcohol, 403
—, — lead tetraethyl, 823
—, — olefins, 604-606
—, — sodium phenolate, 784, 785
—, — styrene, 606
—, resins from, 890, 1047
—, stabilizing agent for methyl chloride, 727
Phenol-aldehyde resin, corrosion inhibitor, 517
Phenolates, as antioxidants, 933
—, effect on color stability, 927
—, for hydrogen sulphide removal, 458
—, reaction with halides, 825
Phenols, alkylation of, 383, 603-607
—, as antioxidants, 906, 914, 936
—, as antiseptics, 825
—, combustion of, 999
—, effect on color stability, 925
—, —, naphthenes, 937
—, — viscosity of asphalts, 1218
—, from chlorobenzenes, 782
—, from cracked oils, 135
—, from naphthalene, 953
—, from primary tars, 729
—, from pyroschists, 145
—, from spent doctor solution, 476
—, in asphalt composition, 1214
—, in crude oil, 10
—, in fungicides, 1112, 1113
—, in insecticides, 1112, 1113
—, in pressure distillates, 1104
—, inhibitors, polymerization of chloroprene, 681
—, oxidation of, 849, 920, 931
—, reaction with alcohols, 402, 412, 416
—, — amines and formaldehyde, 891
—, — naphthenic acids, 1112, 1113
—, — olefins, 383, 412, 606
—, — wax acids, 975
—, resins from, 825
Phenols, separation from asphalts, 1192
—, wetting agents from, 1076
Phenoxazine, as antioxidant, 917
Phenyl, from bromobenzene, 827
Phenyl acetate, from phenol, 438
Phenylacetyl amine, extraction agent for aldehydes, 408
Phenylacetyl chloride, reaction with cyclohexene, 613
Phenylacetylene, from bromostyrenes, 722
—, oxidation of, 904
—, reaction with ethyl hypochlorite, 626
a Phenylacrylic acid, from acetophenone, 451
Phenylallene, preparation of, 807
Phenylazocatechol, as antioxidant, 916
Phenyl bromide, *see* Bromobenzene
1-Phenylbutadiene, effect of lead tetraethyl on, 1022
—, polymerization of, 649
—, reaction with hydrogen halides, 686
2-Phenylbutadiene, preparation of, 678
Phenyl chloride, *see* Chlorobenzene
1-Phenyl-3-chloro-1-butene, from 1-phenylbutadiene, 686
Phenylcyclohexane, from benzene, 207
1-Phenyl-1-cyclohexene, reaction with ozone, 902
Phenylcyclopentane, amylbenzene from, 92
—, autoxidation of, 907
—, pyrolysis of, 91, 92
Phenyl diselenocyanate, as antiknock, 1018
Phenylenediamine, as antioxidant, 917, 927
m-Phenylenediamine, reaction with ethylene oxide, 560
m-Phenylenedi-(β-sulphoethyl) disulphone, preparation of, 618
Phenyl ethers, alkylation of, 606
—, from phenolates, 825, 957
Phenylethyl alcohol, preparation of, 563, 565
Phenylethyl ether, *see* Phenetole
2-(2′-Phenyl) ethylcyclohex-2-en-1-one, from 1-(2′-phenyl)-ethylcyclohexene-1, 619
Phenylethylene, *see* Styrene
Phenylethylene glycol, oxidation of, 536
Phenylglyceric acid, from cinnamic acid, 547, 895
Phenylglyoxal, from acetophenone, 853
Phenylhydrazine, reaction with β,β′-dichlorodiethyl ether, 583
—, — ketones, 448
Phenylic process, for cracking, 131
Phenyl isopropyl ketone, preparation of, 444
Phenylmagnesium chloride, reaction with ethylene dichloride, 565
Phenylmethyl ether, *see* Anisole
Phenylmorpholine, dyes from, 585
—, preparation of, 583
Phenyl-α-naphthylamine, as antioxidant, 918, 936
Phenyl-β-naphthylamine, as antioxidant, 917
—, reaction with acetone, 429
Phenylnitromethane, preparation of, 1091
1-Phenylpentane, *see* Amylbenzene
Phenylphenol, from chlorobenzene, 784, 785
2-Phenyl-1,3-propanediol, from styrene, 625
—, methylene ether, from styrene, 625
Phenylpropiolic acid, reaction with ozone, 904
Phorone, from acetone, 878
Phosgene, absorption by hexamethylenetetramine, 885
—, from carbon tetrachloride, 732, 733
—, from tetrachloroethane, 744
—, reaction with naphthenes, 445
—, — olefins, 609, 611
—, — paraffins, 445, 1101
Phosphates, catalysts, polymerization of aldehydes, 579
Phosphatides, as antioxidants, 915
Phosphine, estimation in ethylene, 1259
—, oxidation of, 851
—, removal from acetylene, 170
Phosphoric acid, absorption of hydroxy acids by, 977
—, catalyst, alkylation of alcohols, 606
—, —, — aromatics, 593, 594
—, —, — phenols, 603, 605
—, —, cracking, 112, 114, 1253
—, —, depolymerization of hydrocarbons, 1040
—, —, esterification of ethylene, 304, 305
—, —, — ethylene glycol, 540
—, —, ethyl alcohol from ether, 333, 334

Phosphoric acid, catalyst, ethylation of amines, 346
—, —, hydration of acetylene, 713
—, —, — olefins, 282, 288, 291, 293, 358
—, —, isomerization of 1-butene, 82
—, —, nitration of acetic anhydride, 1090
—, —, oxidation of olefins, 844, 893, 894
—, —, polymerization of aldehydes, 579
—, —, — Kogasin, 1255
—, —, — olefins, 634, 636, 637, 639, 642, 645, 662-664 672
—, —, reaction of alcohols and isobutene oxide, 589
—, —, — alcohols and phenols, 412, 416
—, —, — carbon monoxide and alcohols, 407, 1050
—, —, — carbon monoxide and olefins, 625, 626
—, —, — chlorobenzene and ammonia, 786, 787
—, —, — ethyl alcohol and hydrogen chloride, 345
—, —, — ethylene and cracked gasoline, 1252, 1253
—, —, — glycols and formaldehyde, 543
—, —, — methane and carbon dioxide, 870
—, —, — methane and steam, 278
—, dehydration agent for alcohols, 400, 406
—, desulphurizing agent, 1044
—, in cleaning agents, 543
—, reaction with ethylene, 323
—, — nitroparaffins, 1096
—, refining agent for biphenyl, 193
Phosphoric anhydride, *see* Phosphorus pentoxide
Phosphorous acid, catalyst, oxidation of paraffin wax, 973
—, —, polymerization of olefins, 634
Phosphorus chlorides, catalysts, chlorination of ethylene, 495
—, —, — propene, 507
Phosphorus compounds, autoxidation of, 905
—, catalysts, reaction of olefins and carbon monoxide, 626
Phosphorus oxychloride, catalyst, alkylation of alcohols, 606
Phosphorus oxyhalides, catalyst, polymerization of olefins, 634
Phosphorus pentabromide, catalyst, bromination of toluene, 795
—, reaction with 1,3-cyclohexadiene, 589
Phosphorus pentachloride, catalyst, fluorination of chloromethane, 735, 736
—, —, nitration of acetic anhydride, 1090
—, reaction with methylcyclohexanol, 775
—, — methyl ethyl ketone, 452
—, — 1-pentene, 511
Phosphorus pentafluoride, catalyst, polymerization of isobutene, 642
Phosphorus pentoxide, as antioxidant, 937
—, catalyst, alkylation of aromatics, 594, 595
—, — polymerization of olefins, 637, 643, 645, 665
—, reaction with acetone cyanohydrin, 428
—, refining agent for gasoline, 669
—, sweetening agent, 475
Phosphorus tribromide, reaction with cyclohexanol, 770
—, — cyclopentanol, 764
Phosphorus trichloride, catalyst, condensation of cyclohexane, 205, 1102
Phosphorus trisulphide, reaction with citric acid, 484
Photochemical decomposition, of hydrocarbons, 264-268
—, of ketones, 448-450
—, of organic lead compounds, 1022
Phthalic acid, from crude oil, 21
—, in demulsifying agents, 946, 947
—, reaction with glycols and alcohols, 542
—, solubility in polar compounds, 959
Phthalic anhydride, ammonium phthalate from, 958
—, benzaldehyde from, 950
—, benzoic acid from, 950-952
—, benzoyl chloride from, 952
—, decarboxylation of, 950-952
—, decolorization of, 958
—, drying agent for *ter*-butyl alcohol, 417
—, from fluorene, 954, 955
—, from kerosene, 966
Phthalic anhydride, from naphthalene, 861, 946, 950
—, in demulsifying agents, 946, 947
—, in dyes, 946
—, phthalyl chloride from, 731, 732
—, reaction with benzotrichloride, 794, 816
—, — butyl alcohol, 501
—, — carbon monoxide, 950
—, — carbon tetrachloride, 731, 732
—, — ethanolamine, 958
—, — ethylene glycol, 541
—, — methyl alcohol, 952
—, — paraffins, 1101
—, — steam, 952
—, — thionyl chloride, 945
—, resins from, 946
—, separation by polymerization, 960, 961
Phthalide, reaction with chlorobenzene, 789
Phthalimide, as antioxidant, 915
—, from ammonium phthalate, 958
Phthalones, from nitrogen bases, 834, 836
Phthalyl chloride, from phthalic anhydride, 731, 732, 794, 816
Picene, in petroleum coke, 145
Pickling inhibitors, aliphatic acids in, 1041
—, petroleum bases as, 841
Pickling solutions, aldehydes in, 890
—, hexamethylenetetramine in, 890
Picolines, as antioxidants, 917
α-Picolyalkine, *see* 2-(2′-Pyridyl) ethanol
Picric acid, catalyst, hydration of olefins, 297, 410
—, reaction with naphthalenes, 36
Pinacol, oxidation of, 536
Pinacolyl alcohol, dehydration of, 645
Pinene, as antiknock, 923, 1017
—, oxidation of, 855, 905
—, polymerization of, 645
—, pyrolysis of, 87, 88
—, reaction with formaldehyde, 624
—, — selenious acid, 446
—, stabilizing agent for methylene chloride, 728
Pinene hydrochloride, utilization of, 758
Pine oil, in lubricants, 1114
—, in motor fuel, 1035
Piperidine, extraction agent for asphalts, 1202
—, reaction with bromocyclohexane, 772, 773
—, — chlorocyclohexane, 768
—, — ethyl alcohol, 346
Piperonyl alcohol, preparation of, 958
Piperylene, from alcohols, 173
—, from kerosene, 144, 171
—, in gasoline, 144
Pitch, from petroleum, 7
—, removal with sulpho detergents, 1084
Pivalic acid, esterification of, 407
Plasticizing agents, alcohols as, 1112
—, ethylene glycol ethers in, 543, 544
—, from paraffin wax, 759, 1054
—, from polymer gasoline, 675
—, naphthenic esters as, 1112, 1120
Plastics, from ethylene dichloride and polysulphides, 499, 828
—, — and sodium thiosulphate, 829
—, from paraffin oil acids, 969
—, from sulphur chloride and olefins, 618, 619
—, wax acids in, 975
—, *see also* Resins
Platinum, catalyst, dehalogenation of haloalkyl ethers, 551
—, —, dehydrogenation of cyclohexane, 92, 179, 185
—, —, — hydrindenes, 95
—, —, — naphthenes, 31, 1150
—, —, ethers from acetals, 715
—, —, hydration of ethylene, 291
—, —, hydrogenation of carbon monoxide, 1049
—, —, — toluene, 347
—, —, — unsaturates, 1153, 1154
—, —, hydrolysis of chlorobenzene, 782
—, —, oxidation of aliphatics, 850, 851, 869, 1129
—, —, — aromatics, 942
—, —, — methane-ammonia mixture, 871
—, —, polmerization of olefins, 665
—, —, pyrolysis of 2-butene, 172
—, —, — ethylidene diesters, 718

Platinum, catalyst, pyrolysis of Kogasin, 155
—, —, — methane, 53
—, —, reaction of acetylene and amines, 719
—, —, — carbon and hydrogen, 1278
—, —, — methane and ammonia, 281
—, —, — nitric oxide and paraffins, 1091
—, —, sulphation of propene, 358
Platinum chloride, reaction with ethyl alcohol, 628
Platinum cyanide, catalyst, sulphation of isobutene, 391
Platinum halides, catalysts, hydrogen fluoride-dichloroethane reaction, 747
—, reaction with unsaturates, 628
Platinum-iridium alloy, catalyst, methane-nitric oxide reaction, 281
Platinum oxide, catalyst, hydrogenation of olefins, 899
—, —, oxidation of *d*-α-pinene, 905
Platinum-palladium, catalyst, oxidation of hydrocarbon gas, 851
Platinum-rhodium, catalyst, oxidation of hydrocarbon gas, 851
Platinum salts, catalysts, hydration of acetylene, 712
—, —, sulphation of isoolefins, 308
Polishing compositions, preparation of, 731, 1079
Polyalkene glycols, reaction with phthalic acid, 542
Polyamines, as antioxidants, 917
Polybasic acids, reaction with polyhydric alcohols, 541
Polybutyl amine, as antioxidant, 915
Polycarboxylic acids, as antioxidants, 941
—, from olefins, 629
—, plasticizing agents from, 542
Polychlorobenzene, chlorination of, 780, 781
—, from monochlorobenzene, 780, 781
—, in dyes, 782
Polychloroprene, chlorination of, 682
—, decomposition of, 682
—, properties of, 681
Polycyclic groups, effect on lubricating oil viscosity, 37
Polyethylene glycols, in cleaning agents, 545
—, esters and ethers in refrigerants, 545
—, solvent properties of, 545
Polyethylene oxides, structure of, 563
Polyethylene sulphone, properties of, 617
Polyglycerols, as lubricants, 545
Polyglycol arsenites, utilization, 545
Polyglycols, reactions of, 545
Polyhalogenated olefins, reaction with hypochlorous acid, 523
Polyhydric alcohols, from paraffin halides, 756
—, in emulsifying agents, 1074
—, oxidation of, 548
—, reaction with aldehydes, 544
—, — polybasic acids, 541, 542
Polyhydroxybenzenes, as antioxidants, 906, 918
—, effect on color stability, 926
Polymer gasoline, antiknock rating, 654
—, by catalytic processes, 662-666
—, by multi-stage process, 661, 662
—, by single-stage process, 656-658
—, by thermal process, 655
—, by two-stage process, 658-661
—, by Unitary process, 658, 659
—, from cracking gas, 97, 146
—, from Kogasin, 1255
Polymerization, during aquolization, 131
—, effect of catalysts, 633
—, in refining gasoline, 928, 929
—, of acetylene, 57, 89, 264-266, 680, 702, 703, 722
—, of aldehydes, 886, 889, 890
—, of alkyl halides, 811
—, of butadiene, 57, 387, 389, 650-652, 1116
—, of butenes, 81, 82, 386, 641-643, 895
—, of *ter*-butylethylene, 643, 645
—, of chloroprene, 681
—, of cyclohexene, 204, 645
—, of cyclopentadiene, 652, 654
—, of deuterioacetylene, 266, 725
—, of dichlorinated Kogasin, 814
—, of 1,2-dichlorobutadiene, 687
Polymerization, of dichlorobutene, 685
—, of *unsym*-dimethyl allene, 88, 650
—, of ethylene, 265, 283, 288, 290, 321, 646, 1041
—, of formaldehyde, 877, 887
—, of hexene, 643
—, —, free energy change, 1299, 1300
—, of isobutene, 296, 390, 633, 641-643
—, —, free energy change, 1300
—, of isopropylethylene, 387
—, of Kogasin, 1255
—, of methylallene, 649, 650
—, of methylisopropylethylene, 643, 645
—, of 3-methyl-2-pentene, 643
—, of olefins, 76, 107, 149, 160, 209, 395, 1041, 1252
—, of 2-pentene, 643
—, of 1-phenylbutadiene, 649
—, of pinene, 645
—, of propene, 288, 639-641
—, of propenylbenzene, 648, 649
—, of styrene, 647, 648, 805
—, of telluroformaldehyde, 51
—, of tetramethylethylene, 643, 645
—, of trimethylethylene, 203, 633
—, of unsaturates, 37
—, of vinylacetylene, 705
—, of vinylethinylcarbinol, 708
—, mechanism of, 631-633
Polymerized hydrocarbons, extraction from acid liquors, 397
Polymethylene alcohols, esterification of, 1118, 1119
Polynuclear hydrocarbons, in crude oil, 13
Polyolefin glycol ethers, solvents for nitrocellulose, 558
Polyoxymethylene, from formaldehyde, 877
Polyphenols, as antioxidants, 917
Polypropene sulphone, reactions of, 618
Polystyrene, depolymerization, 647
—, motor fuel from, 1040
—, preparation of, 647
Polysulphides, preparation of, 481, 482, 526
—, properties of, 482, 483
Polysulphones, preparation of, 618
Polythiophanes, preparation of, 484
Porcelain, catalyst, pyrolysis of ethyl alcohol, 155
—, —, — methane, 54, 180
—, —, reaction of propene oxide and ammonia, 587
Porphyrins, occurrence, 12, 20
Potassium, estimation in lubricants, 1164, 1165
Potassium acetate, catalyst, acetylation of cinnamaldehyde, 439
—, dehydration agent for ethyl alcohol, 329
—, from propene, 629
Potassium-alum, dehydration agent for *n*-propyl alcohol, 379
Potassium aluminate, catalyst, oxidation of toluene, 949
—, —, reaction of propene and metal hydroxides, 894, 895
Potassium amide, reaction with halobenzenes, 787, 810
—, — sulphur, 469
Potassium bisulphite, reaction with vinyl sulphone, 618
Potassium carbonate, catalyst, cracking, 112
—, —, ethyl acetate from ethyl alcohol, 340
—, —, oxidation of ethylene, 894
—, —, reduction of acetone, 432
—, —, — carbon dioxide, 1242
—, —, — carbon monoxide, 1223, 1228, 1231
—, in asphalt emulsions, 1216
—, reaction with ethylene dibromide, 532
Potassium chlorate, catalyst, hydroxylation of olefins, 532
—, —, reaction of chlorobenzene and ammonia, 787
Potassium chloride, catalyst, cracking, 112
—, —, oxidation of propane, 848, 873
—, —, reaction of benzene and dichloropentamethylenetetramine, 779
—, effect of ignition temperatures, 986, 987
—, in refining gasoline, 216
—, recovery from sylvanite solutions, 1063
—, solubility in isopropyl alcohol, 370

Potassium cresolate, reaction with chlorinated paraffins, 807
Potassium cyanide, reaction with potassium ethylene trichloroplatinate monohydrate, 628
Potassium dichromate, catalyst, oxidation of alcohols, 1057
—, —, — anthracene, 954
—, —, — glycols, 537, 546, 548
—, —, — methane, 870
Potassium ethylene trichloroplatinate monohydrate, reactivity of, 628
Potassium ferricyanide, for hydrogen sulphide removal, 1249
Potassium ferrocyanide, catalyst, chlorination of ethylene, 494
Potassium fluoride, fluorine from, 759
Potassium fluoride, reaction with formic acid, 887
Potassium hydrosulphide, catalyst, acetylene-hydrogen sulphide reaction, 721
Potassium hydroxide, antioxidant, 937
—, catalyst, condensation of acetone, 427
—, —, hydration of acetylene, 714
—, —, — ethylene, 291
—, —, hydrolysis of methyl chloride, 796
—, —, reaction of alcohols and ethylene oxide, 558
—, —, — and vinylacetylene, 706
—, dehydration agent for isopropyl alcohol, 364
—, desulphurizing agent, 434, 477
—, inhibitor, oxidation of ether, 335
—, reaction with alkyl halides, 804, 805
—, — butene chlorohydrin, 548
—, — *sec*-butyl alcohol, 407
—, — *ter*-butyl chloride, 412
—, — cyclohexadiene dibromide, 589
—, — 1,4-dichloro-2-butene, 685
—, — 3,4-dichloro-1-butene, 680, 681
—, — ethylene, 629
—, — ethylene dibromide, 504
—, — hexachlorobutane, 510
—, — hexene chlorohydrin, 589
—, — phenol and chlorobenzene, 788, 789
—, — tetrachlorobutane, 687
—, — tetrahydro-α-naphthol, 906
—, solubility in isopropyl alcohol, 375
Potassium iodide, reaction with butene dibromides, 1146, 1147
—, — tetralin peroxide, 906
—, — triethanolamine, 572
Potassium mercuric iodide, reaction with acetylene, 1123
—, — vinylacetylene, 708
Potassium methionate, preparation of, 820
Potassium nitrate, in heat-transfer media, 861, 862
—, promoter, hydration of isobutene, 294
Potassium oleate, in insecticides, 1059
Potassium permanganate, reaction with crudes, 21
—, — ethylene polymers, 203
—, — lead mercaptides, 475
—, — mercaptans, 1158
—, — olefins, 532
—, — paraffin wax, 974
—, — sulphur, 1161
—, — tetralin, 905
Potassium phenolate, reaction with ethylene dibromide, 505
—, — ethylene dichloride, 500
Potassium phosphate, removal of hydrogen sulphide by, 458
Potassium phthalimide, reaction with dibromocyclohexane, 772
Potassium silicate, promoter, in cracking, 112
Potassium sulphate, in cleaning agents, 1112
—, promoter, in cracking, 112
—, reaction with isopropyl ether, 381
Potassium sulphite, reaction with triiodomethane, 819
Potassium β-sulphoacrylate, preparation of, 820
Potassium thiocyanate, reaction with ethylene oxide, 564
Potassium vanadate, catalyst, oxidation of toluene, 949
Potassium vanadyl vanadate, catalyst, oxidation of toluene, 949
Pour point, definition of, 1176, 1177
Pour point depressor, from chlorinated wax, 758, 817
—, from paraffin wax, 215
Praesodymium oxide, catalyst, oxidation of aromatics, 942
Preservatives, *ter*-butyl phenols as, 818
—, copper naphthenates as, 1116
—, from chlorobenzenes, 782
Pressure, effect on cracking, 138, 139
—, — free energy change, 1296, 1298, 1299
—, — heat content, 1329
—, — ignition temperature, 992-996
—, — inflammability limits, 980
—, — polymerization of ethylene, 638, 639
—, — sulphation of ethylene, 299
—, effect on pyrolysis of aliphatics, 156, 188
—, — kerosene, 154
—, — olefins, 185
—, effect on reaction of propene and phosphoric acid, 358
—, increase on combustion, 1002-1005
—, reduced, definition of, 1319
—, relation to fugacity, 1322, 1323
Pressure-enthalpy-temperature relations, 1332, 1335
Pressure-volume product change, relation to heat content change, 1274
Pressure-volume-temperature relations, of hydrocarbons, 1320-1322
Printing ink, carbon black in, 250
—, naphthenates in, 1117
Progressive degradation method, for determination of naphthenic acids, 1104, 1111
Proofing agents, triethanolamine in, 577
Propadiene, *see* Allene
Propane, acetylene from, 61, 166, 168, 169, 187, 254
—, acids from, 858, 859, 862, 863
—, alcohols from, 858, 862, 863
—, aldehydes from, 858, 862, 863
—, aromatics from, 60, 61, 172, 181, 182
—, as motor fuel, 26, 1040
—, carbon black from, 219
—, chlorinated, utilization of, 751
—, combustion of, 241, 1003, 1004
—, commercial, specifications, 25
—, cracking of, 100, 101
—, cyclopentadiene from, 60, 182
—, energy of activation of, 58
—, entropy-temperature relations of, 1337-1340
—, estimation of, 1131, 1132
—, extraction agent, 31, 45, 262, 972, 1071, 1205
—, from *n*-butane, 201
—, from coke-oven gas, 165
—, from cyclopentane, 90
—, from gas oil, 140
—, from gasoline, 24
—, from hexadecane, 202
—, from hexane, 71, 257
—, from isobutene, 84
—, from isopentane, 69
—, from methane, 263
—, from methyl ethyl ketone, 449
—, from *n*-pentane, 68
—, from propylbenzene, 208
—, heat of combustion of, 15
—, hydrogen from, 60, 149, 275
—, ignition temperature of, 988, 989, 992, 993
—, inflammability limits of, 980, 984
—, inhibitor, decomposition of ethylene oxide, 554
—, in natural gases, 21, 22
—, ketones from, 858, 862
—, liquid hydrocarbons from, 160
—, methane from, 60, 151, 169
—, olefins from, 58-61, 149-153, 158, 160, 169, 873, 1284
—, oxidation of, 848, 850, 851, 858, 859, 862, 863, 869, 872-874
—, precipitant, 42, 45, 46, 1201
—, pyrolysis of, 57-61, 148-153, 158, 160, 166, 172, 181, 182, 555
—, reaction with chlorine, 749, 750
—, — ethylene, 601
—, — nitric acid, 1087
—, — steam, 275, 280

Propane, styrene from, 60, 182
—, utilization of, 25-27
1,2-Propanediol, oxidation of, 549
Propanol, *see* Propyl alcohol
Propanolamines, extraction agents for carbon dioxide, 587
—, — ethylene, 164
Propene, acetone from, 173, 292
—, acetylene from, 81, 187
—, allene from, 75
—, aromatics from, 639
—, as anesthetic, 1263
—, as motor fuel, 1040
—, butadiene from, 81
—, butene from, 641
—, chlorination of, 493
—, chlorohydrin from, 518
—, docedenes from, 639
—, effect on ethylene-sulphuric acid reaction, 324
—, — pulse rate, 1263
—, estimation in cracked gases, 1142
—, ethane from, 80
—, ethylene from, 80, 639
—, extraction of, 162, 163, 323, 324
—, from *n*-butane, 62-64
—, from carbon monoxide and hydrogen, 1241
—, from cyclohexane, 93
—, from cyclopentane, 90
—, from ethyl alcohol, 155
—, from ethylene, 636
—, from gas oil, 140
—, from gasoline, 136
—, from hexane, 257
—, from isobutane, 66
—, from isobutene, 85
—, from isopentane, 69
—, from isopropyl alcohol, 173, 365, 377
—, from isopropyl sulphate, 363
—, from ketones, 450
—, from methylcyclopentane, 90
—, from paraffin wax, 138
—, from *n*-pentane, 68
—, from 2-pentene, 87
—, from propane, 58-60, 149, 151, 153, 873
—, —, free energy change, 1284
—, from *n*-propyl alcohol, 173
—, hexenes from, 75, 79, 639, 641
—, hydration of, 288, 291-293
—, —, heat, 293
—, hydrogen from, 79, 81
—, ignition temperature of, 988
—, in commercial propane, 25
—, isobutyric acid from, 626
—, isopropyl alcohol from, 895
—, isopropyl mercaptan from, 462
—, methane from, 80
—, methyl radical from, 79
—, naphthenes from, 639
—, nonenes from, 639
—, oxidation of, 553, 629
—, paraffins from, 639
—, pentadecenes from, 639
—, pentenes from, 79, 641
—, polymerization of, 288, 639-641, 895
—, propene nitrosite from, 620
—, properties of, 15
—, *n*-propyl alcohol from, 292
—, *n*-propyl mercaptan from, 462
—, pyrolysis of, 75, 76, 79-81, 184, 187, 555
—, —, mechanism, 79
—, reaction with acetic acid, 307, 308, 359
—, — acetyl chloride, 612
—, — alkali hydroxides, 629, 894
—, — benzene, 591-593, 595-597
—, — benzoic acid, 308
—, — *ter*-butyl hypochlorite, 518
—, — carbon monoxide, 626
—, — chlorine and water, 516
—, — chloroacetic acid, 308
—, — α-chloromethyl ether, 613
—, — cresols, 605
—, — ethylene chlorohydrin, 529
—, — fluorene, 594
—, — hydrogen bromide, 307, 316
—, — hydrogen chloride, 306
Propene, reaction with hydrogen iodide, 316, 317
—, — hydrogen sulphide, 462
—, — hydroxy-benzoic acid, 609
—, — naphthalene, 593, 594, 596
—, — naphthalene sulphonic acid, 593
—, — nitrogen trioxide, 620
—, — phenol, 603, 604, 606
—, — phosphoric acid, 358
—, —, salicylic acid, 308, 607, 609
—, — stearic acid, 588
—, — sulphur dioxide, 617
—, — sulphuric acid, 161, 305, 306, 323, 356, 357, 359, 362, 363, 391, 1142
—, — sulphuric acid, mechanism, 357
—, — toluene, 594, 596
—, vinyl radical from, 75, 79
Propene chlorohydrin, from propene, 518
Propene dibromide, from propene, 508
Propene dichloride, azeotropic mixture with water, 507
—, 1-chloro-1-propene from, 508
—, dewaxing agent, 495, 507
—, drying agent for acids, 507
—, from propene, 506
—, in insecticides, 507
—, in lacquers, 751
—, paint remover, 507, 790
—, propene glycol from, 546
—, reaction with sodium cyanide, 507
—, solvent for cellulose acetate, 415
—, — cellulose acetopropionate, 507
—, — vinyl resin, 507
—, trichloropropane from, 508
—, *see also* 1,2-Dichloropropane
Propene dinitrate, preparation of, 587
Propene dinitrin, preparation of, 587
Propene glycol, dehydration agent, 538
—, estimation of, 537, 546
—, fatty acid esters, toxicity of, 549
—, from butyl lactate, 546
—, from glycerol, 547
—, from propene, 553
—, from propene dichloride, 546
—, hydroxy ketone from, 536
—, in brake fluid mixtures, 539
—, in cosmetics, 549
—, in heat transfer medium, 539
—, oxidation of, 536
—, properties of, 547
—, reaction with potassium dichromate, 537
Propene glycol carbonate, preparation of, 524, 525
Propene glycol formal, as solvent, 542, 543
Propene nitrosite, from propene, 620
Propene oxide, aldehydes from, 586
—, allyl alcohol from, 586
—, dimethyldioxane from, 579
—, from propene, 553, 586
—, hydrogenation of, 586
—, in adhesives, 586
—, polymerization of, 562
—, reaction with amines, 587
—, — ammonia, 585, 587
—, — cellulose phthalate, 588
—, — cetyl alcohol, 587
—, — diethyl magnesium, 586
—, — ethyl magnesium bromide, 586
—, — metal halides, 560
Propene sulphone, reaction with barium hydroxide, 617
Propenylbenzene, polymerization of, 648, 649
—, reaction with methyl hypobromite, 531
Propenylbenzoic acid, reaction with ozone, 902
p-Propenylmethoxybenzene, *see* Anethole
Propionaldehyde, decomposition of, 884
—, effect on ignition temperatures, 993
—, extraction agent, 44
—, from propene, 553
—, from propene oxide, 586
—, from *n*-propyl alcohol, 173
—, ozonization of, 887
Propionic acid, anhydration with propene chloride, 507
—, effect on sulphation of propene, 357
—, from *sec*-butyl alcohol, 407

Propionic acid, from carbon monoxide and hydrogen, 1244
—, from ethyl alcohol, 339
—, from ethylene, 446, 626
—, from methylethylacetylene, 904
—, from methyl ethyl ketone, 452
—, from paraffin wax, 971
—, from propene, 553
—, from sapropelite tar, 145
Propionitrile, extraction agent, 44
Propionyl chloride, reaction with *n*-propylbenzene, 447
Propyl acetate, extraction agent for polymerized hydrocarbons, 397
—, from propene, 308
Propyl alcohol, as antiknock, 1017
—, 1,3-dimethylbutadiene from, 173
—, esters from, 339
—, ethylene from, 173
—, extraction agent, 681, 1200
—, from pentane, 859, 864
—, from propene, 292
—, from propene oxide, 586
—, inflammability limits of, 980, 981
—, methyl-2-pentene from, 173
—, octane number of, 1028
—, propene from, 173
—, propionaldehyde from, 173
—, propyl ether from, 379
—, reaction with phenol, 384
—, stabilizing agent for tetrachloroethane, 743
Propylbenzene, from cyclohexanes, 94
—, from propenylbenzene polymer, 649
—, from sapropelite tar, 144
—, indene from, 156
—, reaction with propionyl chloride, 447
Propyl bromide, from propene, 307, 316
—, isomerization of, 316
Propyl chloride, dechlorination of, 805
—, from cracking gas, 302
Propylcyclohexane, from cyclohexanes, 93, 94
—, pyrolysis of, 91
Propylcyclopentyl carbinol, preparation, 765
Propyl disulphide, effect on color stability, 456, 924
Propyl ether, from propyl alcohol, 379
Propyl fluoride, from propene, 307
Propyl mercaptan, effect on color stability, 454
—, from propene, 462
—, reaction with cyclohexene oxide, 472
p-Propylpropiophenone, preparation of, 447
Propyl sulphide, preparation of, 479
Proteins, petroleum from, 19
—, precipitation with formaldehyde, 890, 891
Prussian-blue coloration, detection of alcohols by, 371
Pseudocritical points, definition of, 1318
—, determination of, 1318, 1319
Pseudocumene, from acetylene and benzene, 719
—, from kerosene, 36
—, from sapropelite tar, 144
—, from xylenes, 208
—, in crude oil, 35
Pseudonitroles, from nitroparaffins, 1093
—, reaction with aniline, 1094
Pseudonitrosite, from stilbene, 621
Pseudo-unimolecular reaction, definition of, 96
Pulse, effect of propene on, 1263
Pumice, catalyst, chlorination of methane, 726
—, —, decarboxylation of phthalic anhydride, 951
—, —, dechlorination of ethyl chloride, 805
—, —, esterification of ethyl alcohol, 304
—, —, in cracking, 144
—, —, pyrolysis of natural gas, 223
—, —, reduction of carbon monoxide, 1241
—, drying agent for *sec*-butyl alcohol, 400
Pyrazine, from cottonseed meal, 840
—, from ethanolamine, 568
Pyrene, action of aluminum chloride on, 215
—, chlorination of, 956
—, from natural gas, 220, 240
Pyrethrum, in insecticides, 1078
Pyridine, as antioxidant, 917
—, catalyst, hydration of olefins, 282
—, —, hydrolysis of vinyl acetate, 553
Pyridine, catalyst, oxidation of oils, 1044
—, —, reaction of ethylene dichloride and sodium acetate, 499
—, —, — mercaptans and ketones, 474
—, —, — vinylacetylene and hydrogen sulphide, 709
—, —, sulphation of alcohols, 1085
—, extraction agent, 977
—, for hydrogen sulphide removal, 458, 459
—, from cottonseed meal, 840
—, from petroleum, 833
—, peptizing agent for asphalts, 1196
—, reaction with monochlorocyclohexane, 768
—, — potassium ethylene trichloroplatinate monohydrate, 628
Pyridine bases, from acetylene, 719
—, from aldehydes, 885, 886
—, from pyroschists, 145
Pyridine homologues, from petroleum, 838
Pyridine oleate, in motor fuels, 1038
2-(2′-Pyridyl) ethanol, from 2-methylpyridine, 623
Pyrindane, isolation of, 841
Pyrocatechol, from *o*-dichlorobenzene, 785
—, reaction with methylene chloride, 828
Pyrocatechol ethers, preparation of, 825
Pyrocatechualdehyde, from heliotropin, 496
Pyrogallol, absorption of oxygen by, 1124
—, as antioxidant, 907, 913, 914, 916, 917
—, catalyst, hydrolysis of alkyl halides, 797, 801
—, decomposition of, 1124
—, effect on color stability, 926
—, inhibitor, polymerization of vinylacetylene, 705
Pyrogenesis, origin of petroleum, 17
Pyrolysis, effect of reaction chambers, 58, 63, 151-153, 159, 160, 188
—, free radicals from, 50-52
—, of acetals, 341
—, of acetylene, 88, 89
—, of allylcyclohexane, 93
—, of allylcyclohexene, 94
—, of allyltoluene, 96
—, of benzene, 95
—, of *n*-butane, 61-63, 150, 152
—, —, mechanism, 61, 62
—, of *n*-butenes, 81
—, of butylcyclopentanes, 91
—, of cracking gas, 136
—, of cyclohexane, 92, 93
—, of cyclohexylallene, 94
—, of cyclohexylallylene, 94
—, of cyclopentane, 90
—, of cylinder oil, 137
—, of diallyl, 88
—, of di-*ter*-butylethylene, 87
—, of dichlorobutanes, 678
—, of diisobutylene, 87
—, of 2,6-dimethylanthracene, 96
—, of dimethylcyclohexane, 93
—, of 2,5-dimethylhexane, 72
—, of esters, 340
—, of ethane, 55, 56, 150, 151, 158
—, of ethyl acetate, 341
—, of ethyl alcohol, 331, 347-353
—, of ethylbenzene, 95, 96
—, of ethylcyclohexane, 91
—, of ethylene, 56, 77
—, of ethylidene diacetate, 718
—, of gasoline, 154, 178, 179
—, of heptane, 71, 154
—, of *n*-hexane, 69-71, 154
—, of isoamylcyclopentane, 91
—, of isobutane, 65
—, of isobutene, 84, 85
—, of isopentane, 68, 69, 154
—, of kerosene, 137, 154, 155, 171
—, of Kogasin, 73, 155
—, of mercaptans, 479
—, of methane, 52, 53, 149, 158
—, of methylallene, 88
—, of methylcyclohexane, 91
—, of methylcyclopentane, 90, 91
—, of natural gas, 158-160
—, of nonane, 72
—, of octadecane, 73

Pyrolysis, of *n*-octane, 72
—, of *n*-pentane, 67, 149, 154
—, of pentenes, 85-87
—, of phenylcyclopentane, 91, 92
—, of pinene, 87
—, of propane, 57-59, 79, 150, 152, 153, 158, 160
—, of propylcyclohexane, 91
—, of spindle oil, 36, 37
—, of thiophene, 483
—, of 2,4,4, trimethyl-2-pentene, 87
—, of vinylcyclohexane, 93
—, of *p*-xylene, 96
—, stability of paraffins during, 49, 50
γ-Pyrone, from carbon monoxide and hydrogen, 1244
Pyrones, from wax acids, 979
Pyrophosphates, catalysts, reaction of ethylene glycol and aldehydes, 889, 890
Pyroschists, cracking of, 145
Pyrosulphates, catalysts, reaction of ethylene glycol and aldehydes, 889, 890
—, —, — glycols and ketones, 582
—, desulphurizing agents, 490, 929
Pyroxylin, solubility in ketones, 433
Pyrroles, extractants for asphalts, 1202
Pyruvic aldehyde, from acetone, 853

Q

Quartz, effect, ignition temperatures, 986
—, —, pyrolysis of methane, 53, 54
—, —, — propane, 58
—, in decarboxylation of zinc phthalate, 952
Quaternary ammonium compounds, from *ter*-alkylolamines, 572
Quinaldine, from acetylene and aniline, 719
—, from petroleum, 838
Quinhydrone, color stabilizer, 926
—, from hydroquinone, 382
Quinoline, catalyst, hydration of olefins, 282
—, for hydrogen sulphide removal, 458, 459
—, from anthracene oil, 839
—, from cottonseed meal, 840
—, from petroleum, 833, 838
—, in preparation of methacrylonitrile, 428
—, — olefins from alkylhalides, 804
—, reaction with dibromocyclohexane, 772
Quinolines, extractants, for asphalts, 1202
Quinone, as antiknock, 1018
—, from benzene, 942
—, from hydroquinone, 1277
Quinoneazine, condensation with cyclopentadiene, 693
Quinone compounds, inhibitors, polymerization of chloroprene, 681
Quinones, antioxidants for naphthenes, 937
—, from naphthalene, 953
—, reaction with diolefins, 175, 679, 688, 689, 699

R

β-Radiations, action on hydrocarbons, 267
Radon, action on cyclopentane, 267
—, — cyclopentene, 267
Raman spectra, determination of, 1181-1183
—, in petroleum analysis, 32
Rangoon paraffin wax, cracking of, 138
Rapeseed oil, cracking of, 136
Rapid-ignition point, definition of, 987
Rate of decomposition, in unimolecular reactions, 50
Rate of solution, of methane in oils, 9
Rayon, action of triethanolamine on, 578
—, viscose, sizing agent for, 587
—, —, softening agent for, 588
—, —, waterproofing of, 569
β-Rays, action on gaseous hydrocarbons, 268
—, — water gas, 268
Recycling, in cracking, 109
Red light, effect on iodine-ethylene reaction, 505
Red oil, as cleansing agent, 790
Reduced copper, removal of acetylene by, 171
Reduced equation of state, 1319
Reduced pressure, definition of, 1319
Reduced temperature, definition of, 1319
Reduced volume, definition of, 1319
Reduction, acetaldol to 1,3-butene glycol, 547
—, of aldehydes, 885, 889
—, of benzoquinone, 953
—, of carbon dioxide, 1247
—, of carbon monoxide, free energy change, 1303-1305
—, of diolefins to monolefins, 698
—, of maleic acid, 945
—, of naphthenic acids, 1118
—, of nitroparaffins, 1094, 1095
Reference standards, in knock rating, 1024-1027
Refining, effect on stability of oils, 940
—, of paraffin wax, 39
—, of petroleum, 31
—, of sulphonates, 1072, 1073
—, use of acetic acid, 625
—, — aldehydes, 625
—, — carbon tetrachloride, 731
—, — clay adsorbents, 135
Refining agent, sulphuric acid as, 1069, 1070
—, for gasoline, 927-930
Refining methods, effect on color stability, 927
Reforming, of naphtha, 105
Refractive index, in analysis of gasoline, 144
Refractivity index, 1178
Refractivity intercept, 1178
Refrigerants, chloroethanes in, 745
—, chlorofluoromethanes, 737
—, chloromethanes in, 727
—, dichlorobenzene in, 790
—, polyethylene glycol derivatives in, 545
Repressuring, with natural gas, 9
Residual oils, oxidized to alcohols, 1050
—, — asphalts, 1043
Residuum tar, motor fuels from, 136
Residuums, characterization factor of, 1308
Resinic acid, glycol ethers from, 543
Resins, adsorption agents for, 1188
—, antioxidants for naphthenes, 937
—, as sizing agents, 1189
—, by chlorination of tar, 756
—, by co-polymerization of olefins and diolefins, 216
—, by oxidation of petroleum, 1057, 1058
—, decolorization of, 216
—, extraction from oils, 1188, 1189
—, from acetylene, 701
—, from aldehydes, 886, 890, 1081
—, from aluminum chloride sludge, 217
—, from chlorinated hydrocarbons, 814, 815
—, from 1-chlorobutadiene, 685
—, from coniferous wood, 46
—, from cracked gasoline, 216, 625
—, from cracking tars, 147
—, from dichlorobutenes, 685
—, from esters of polyhydric alcohols, 541
—, from ethane, 257
—, from ethylene and sulphur chloride, 618, 619
—, from ethylene chlorohydrin, 525, 526
—, from indene, 155
—, from ketones, 453
—, from monovinylacetylene, 685
—, from olefins and aldehydes, 625
—, from olefins and sulphur dioxide, 618
—, from petrolatum and carbon tetrachloride, 732
—, from petrolenes, 1202
—, from phthalic anhydride, 946
—, from polypropene sulphone, 618
—, from primary tars, 729
—, from residual hydrocarbons, 1189
—, from styrene, 155
—, from sulphonic acids, 1081
—, glycol ethers from, 543
—, in alkali sludge, 1105
—, in chewing gum bases, 1189
—, iodine numbers of, 216, 217
—, oil-soluble, preparation of, 818
—, oxidized to asphaltenes, 1189
—, petroleum, uses of, 147
—, reaction with castor oil, 217
—, — glycerol, 217
—, solvents for, 453, 1188
—, substitutes for shellac, 625
Resolution, of azeotropic mixture, 30

Resonance isomerization, definition of, 442
Resorcinol, color stabilizer, 926
—, reaction with ethylene chlorohydrin, 525
—, — acetylene, 715
—, — secondary alcohols, 403, 409
—, stabilizer for methyl chloride, 727
Rhenium, catalyst, dehydrogenation of alcohols, 420
—, inhibitor, decomposition of ketones, 420
Rhenium halides, catalyst, dehydrogenation of hydrocarbons, 158
Rhodanates, as insecticides, 1059
—, preparation of, 1059
Rice mechanism, pyrolysis of neopentane, 69
—, — *n*-pentane, 68
Ricinoleic acid, detergent properties of soaps from, 1113
—, reaction with isobutyl alcohol, 1086
Ring formation, inhibitors of, 138
Roofing compositions, asphalts in, 1213
Rosin, for stabilizing carbon tetrachloride, 730
—, in emulsifying agents, 1114
—, in insecticides, 790
—, purification of, 46
—, reaction with hydrogen sulphide, 466
—, soluble oil from, 538
Rosin soap, in vulcanization of rubber, 1078
Rosin soaps, detergent properties of, 1113
—, in asphalt emulsions, 1218
—, in emulsifying agents, 1079
Rubber, autoxidation of, 905
—, carbon black in, 246, 249
—, channel black in, 250
—, chlorinated, in coating composition, 543
—, di-*n*-propyl ketone, solvent for, 443
—, mastication of, 1078
—, motor fuel from, 136
—, synthetic, from acetylene, 701
—, —, from butadiene, 173, 672, 673, 674
—, —, uses of, 674
—, —, vulcanization of, 674
Rubber, vulcanization of, 468, 1078
Rubber cement, improving film-breaking tendency of, 374
—, reducing viscosity of, 374
Rubber latex, use in asphalt emulsions, 1218
Rubber-like material, from 1,2-dichlorobutadiene, 687
—, from polyprene, 682
Rubber sponge, triethanolamine in manufacture of, 577
Rubidium carbonate, promoter, reduction of carbon monoxide, 1228
Rubrene, oxidation of, 848, 849
Ruthenium, catalyst, reduction of carbon dioxide, 1242

S

Salicylaldehyde, in determination of acetone, 424
Salicylic acid, color stabilizer for gasoline, 926
—, in asphalt emulsions, 1219
—, reaction with ketene, 438
—, reaction with propene, 308, 607, 609
—, solubility of, 959
Samarium oxide, catalyst, oxidation of aromatics, 942
Sand molds, preparation of, 731
Saponifiable substances, adsorption of, 732
Saponification number, determination of, 1166, 1167, 1195
Saponin, use, in cleaning agents, 543
Sapropelite tar, cracking of, 135, 143-145
—, polymerization of olefins from, 211
Sapropels, definition of, 975
—, oxidation of, 975
Saturates, as antiknocks, 1016
Sawdust, use in cracking, 111
Scouring agents, dichloroethane in, 745
—, triethanolamine in, 577
Sea water, bromine from, 504
Sebacic acid, alkoxyalkyl ester, use as plasticizer, 544
Second order reaction, definition of, 501
Selenious acid, use in preparation of unsaturated ketones, 446
Selenious oxide, in oxidation of acetone, 432
Selenium, catalyst, bromination of benzene, 790, 791
—, —, cracking, 113
—, —, pyrolysis of hydrocarbons, 94, 158, 189, 191
—, reaction with acetylene, 720
—, use in lubricants, 469
—, use in refining gasoline, 669
Selenium charcoal, dehydrogenation catalyst, 94
Selenium dioxide, as oxidizing agent, 852, 853, 895, 900, 957
—, reaction with ketones, 853
—, — aromatics, 957
—, — olefins, 895, 900
Selenium oxide, catalyst, oxidation of olefins, 553
Selenium oxychloride, catalyst, oxidation of benzaldehyde, 957
Selenophene, preparation, 720
Semenov's law, 997, 998
Semicarbazides, as antioxidants, 915
Sesquiterpenes, preparation of, 688
Shale oil, aquolysis of, 132
—, green oil from, 242
—, hydrocarbons in, 32, 33, 35
—, medicinal products from, 1080
—, substitute for petroleum, 9
Shale-oil gasoline, *n*-heptane from, 32
Shale-oil tar, carboids from, 1194
—, reaction with sulphuric acid, 1069
Shaving preparations, 540, 1081
Shukhov-Kapelyushnikov cracking process, 123
Silent discharge, action on acetylene, 258
—, — aromatics, 259, 260
—, — olefins, 258, 259
—, — paraffins, 257, 258, 263
—, dehydrogenation by, 256
—, in dewaxing, 263, 264
—, in methane oxidation, 264
—, in vapor-phase cracking, 263
—, polymerization with, 210, 256, 263
—, reduction with, 264
Silica, catalyst, chlorination of toluene, 793
—, —, cracking, 128
—, —, hydrolysis of chlorobenzene, 782, 783
—, —, oxidation of aromatics, 942
—, —, ozonization of gasoline, 1045
—, —, polymerization of olefins, 1042
—, —, pyrolysis of hydrocarbons, 71, 180, 227
—, —, reaction of methane and carbon monoxide, 1050
—, —, — olefins and sulphuric acid, 323
—, —, reduction of carbon monoxide, 1228, 1239, 1240, 1241, 1249
—, impurity in acetylene black, 244
Silica dust, effect, on inflammability limits, 985
Silica gel, catalyst, cracking, 112
—, —, hydrolysis of mesityl oxide, 423
—, —, isomerization of propene oxide, 586
—, —, nitration of benzene, 1092
—, —, oxidation of hydrocarbons, 444, 882, 949
—, —, polymerization of diolefins, 171, 667
—, —, — olefins, 642, 666
—, —, pyrolysis of aliphatics, 189
—, —, — 2-butene, 172
—, —, reaction of acetylene and acetic acid, 717
—, —, — ethyl chloride and carbon monoxide, 830
—, —, — ketene and hydrogen chloride, 439
—, —, — phenol and lead tetraethyl, 823
—, —, — propene and hydrogen halides, 306, 307, 316
—, desulphurizing agent, 398, 489
—, selective adsorbent, 31, 165, 732, 1046, 1155, 1188
Silicates, catalyst, ozonization of gasoline, 1045
—, —, reaction of amines and alcohol, 614
Silicic-acetic anhydride, reaction with acids, 1116
Silicic acid, use in refining gasoline, 669
Silicon, acid salts as catalysts, reaction of olefins and carbon monoxide, 626
—, catalyst, chlorination of benzene, 778
—, —, cracking, 115
—, —, dehydrogenation of acenaphthene, 955

Silicon, catalyst, polymerization of acetylene, 89
—, —, pyrolysis of aliphatics, 189
—, —, — benzene, 191
—, —, — saturated hydrocarbons, 159
—, —, reaction of carbon disulphide and chlorine, 730
—, —, reduction of carbon monoxide, 1228
—, in alloys, to reduce corrosion, 134
Silicon carbide, catalyst, oxidation of naphthalene, 946
—, in pyrolysis reactions, 167, 168, 189, 192
Silicon carboxylates, catalysts, hydrogenation, 1116
Silicon halides, catalyst, dehydrogenation of hydrocarbons, 158
Silicon tetrachloride, in refrigerants, 738
—, reaction with cyclohexane, 1102
Silicon tetrafluoride, fluorinating agent, 736
Silicotungstic acid, catalyst, ethylene oxidation, 894
—, test for nitrogenous substances, 925
Sillimanite, use in dehydrogenation of alcohol, 1051, 1052
Silver, catalyst, combustion of carbon monoxide, 1000
—, —, cracking, 112
—, —, dimerization of acetylene, 705
—, —, ethers from acetals, 715
—, —, ethyl alcohol from ether, 333
—, —, fluorination of benzene, 791
—, —, higher alcohols from ethanol, 340
—, —, hydrolysis of chlorobenzene, 782
—, —, hydrolysis of *o*-dichlorobenzene, 785
—, —, oxidation of alcohols, 420, 421, 844, 878-880, 1051
—, —, — ethylene, 552, 553, 893
—, —, — methane, 869
—, —, — olefins, 552, 553, 586, 893
—, —, — paraffins, 874
—, —, — propene, 586
—, —, sulphation of ethylene, 323
—, —, — propene, 358, 360
—, —, reaction of ketones and alcohols, 443
—, —, reduction of carbon monoxide, 1229, 1241
—, effect, on ignition temperature, 986
—, in estimation of sulphur, 1162, 1163
—, in test for aldehydes, 885
Silver acetate, in preparation of cycloolefin oxides, 589
Silver bromate, solubility in isopropyl alcohol, 370
Silver cyanide, catalyst, preparation of *ter*-butyl alcohol, 391
—, for hydrogen sulphide detection, 466
Silver fluoride, reaction with choloroform and calcium fluoride, 737
Silver halide, catalyst, dehydrogenation of hydrocarbons, 158
—, —, dichloroethane-hydrogen fluoride reaction, 747
Silver hydroxide, reaction with *ter*-bromides, 413
—, stabilizer, for ether, 336
Silver nitrate, extraction agent for butadiene, 174
—, in estimation of acetylene, 1144, 1145
—, — mercaptans, 1158, 1159
—, — sulphur, 1157
—, promoter, hydration of isobutene, 296
—, reaction with asphaltogenic acids, 1195
Silver oxalate, oxidation catalyst from, 553
Silver oxide, carbon monoxide estimation with, 1125
—, catalyst, ketone-alcohol reaction, 443
—, —, oxidation of alcohols, 844
—, —, — methane, 869
—, —, — olefins, 553
—, —, — *d*-α-pinene, 905
—, —, — toluene, 950
—, stabilizer, for ether, 336, 381
Silver perchlorate, catalyst, iodination of cyclohexene, 774
Silver salts, catalysts, hydration of vinylacetylene, 705
—, —, oxidation of toluene, 950
—, —, polymerization of olefins, 634
—, —, sulphation of isoolefins, 308
—, —, — propene, 357, 358
—, effect on stability of lubricants, 938
Silver sulphate, catalyst, hydration of ethylene, 283, 286
—, —, hydration of propene, 291, 292
—, —, reaction of propene and phosphoric acid, 358
—, —, sulphation of butene, 387
—, —, — ethylene, 322, 323
—, —, — propene, 358
—, in estimation of olefins, 1124, 1135
Silver vanadate, catalyst, oxidation of anthracene, 952
Sizing agents, from propene oxide, 587
—, from triethanolamine, 577
—, petroleum resins in, 1189
—, sulphonaphthenic acid salts as, 1118
—, urethans as, 569
Slack wax, polymerization of, 212
Slop wax, extraction of, 972
—, oxidation of, 972
Sludge formation, in oils, 937, 939, 940
Sludge value, of lubricants, determination of, 934
Soap powders, wax acids in, 978
Soaps, from wax acids, 970
—, in asphalt emulsions, 1219
—, in fungicides, 969
—, in insecticides, 969, 1077
—, in lubricants, 968
—, water-insoluble, preparation of, 1055
Soda-lime, as extraction agent, 1106, 1107
—, catalyst, depolymerization, 1040
—, —, polymerization of dichlorobutenes, 685
Sodamide, desulphurizing agent, 489
—, in preparation of ethyl propiolic acid, 511
—, reaction with 1,2-dibromobutane, 829
Sodium, catalyst, alkyl halides-aromatics reaction, 827
—, —, cracking, 113
—, —, ethylene oxide from chlorodimethyl ether, 551
—, —, polymerization of butadiene, 651, 673
—, —, pyrolysis of olefins, 76
—, desulphurizing agent, 489
—, in estimation of lubricating greases, 1164, 1165
—, — sulphur, 1162
—, — water in gasoline, 1168
—, in refining gasoline, 669
—, reaction with alkyl bromides, 826
—, — aryl bromides, 827
—, — *ter*-butyl alcohol, 418
—, — halogenated hydrocarbons, 722
—, — methylacetylene, 722
—, — naphthalene, 957, 958
Sodium acetate, dehydrating agent, 329
—, from ethyl alcohol, 342
—, in estimation of mercaptans, 1159
—, reaction with benzyl chloride and acetic acid, 794
—, — ethylene dichloride, 499
—, to stabilize acetaldehyde, 713
Sodium acetylide, reaction with iodine, 711
—, — methyl iodide, 722
Sodium acid sulphate, catalyst, ethers from *ter*-alcohols, 413, 414
—, —, reaction of ethylene glycol and paraformaldehyde, 582
—, —, — propene and acetic acid, 308
Sodium alcoholates, catalysts, alcohol-vinylacetylene reaction, 705
—, reaction with alkyl halides, 826
Sodium-aluminum-borotitanate, catalyst, decomposition of ether, 335
Sodium amalgam, in reduction of nitrolic acids, 1094
Sodium arsenate, absorption of chlorine by, 744
—, inhibitor, corrosion of iron, 574
Sodium bicarbonate, reaction with ethylene dichloride, 532
—, — propene dichloride, 546
Sodium bisulphite, autoxidation of, 905
—, catalyst, 1,5-dihydroxynaphthalene-ethanolamine reaction, 569
—, —, oxidation of petroleum, 966
—, reaction with ethylene oxide, 565
—, — ketones, 448

Sodium bisulphite, reaction with tetralin peroxide, 906
—, — vinyl sulphones, 618
Sodium borate, effect on asphalt emulsions, 1216
Sodium *ter*-butylate, formation of, 418
Sodium carbonate, catalyst, cracking, 112
—, —, oxidation of paraffin wax, 971
—, — reduction of carbon monoxide, 1229
—, effect on asphalt emulsions, 1216
—, — naphthenic acid soaps, 1113
—, extraction agent, naphthenic acids, 1105, 1107
—, inhibitor, dehydration of alcohols, 420
—, reaction with ethylene chlorohydrin, 533, 534
—, — ethylene dichloride, 532, 533
—, — propene dichloride, 546
—, sulphur estimation by, 1127
Sodium chloride, as demulsifying agent, 1108, 1111, 1112
—, catalyst, cracking, 112
—, —, decarboxylation of phthalic anhydride, 950
—, effect on asphalt emulsions, 1215, 1216, 1218
—, — methane pyrolysis, 54
—, in estimation of olefins, 1143
—, in refining of gasoline, 216
—, in refining of isopropyl alcohol, 365
—, solubility in isopropyl alcohol, 370
Sodium copper silicate, catalysts, hydrolysis of chlorobenzene, 783
Sodium cyanide, reaction with amyl chloride, 822
—, — olefins, 305
—, — propene dichloride, 507
Sodium deutroxide, reaction with chloral deuterate, 729
Sodium diphenylmethyl, catalyst, polymerization of butadiene, 651
Sodium ethoxide, catalyst, reaction of mercaptans and ketones, 474
Sodium ethyl sulphonate, preparation of, 819
Sodium formate, in hydrolysis of *o*-dichlorobenzene, 785
Sodium hydride, catalyst, cracking, 115
Sodium hydrosulphide, oxidation of, 465
—, reaction with mercaptans, 480
Sodium hydroxide, bromine absorption by, 1143
—, catalyst, condensation of acetone, 427
—, —, — dichlorobutenes, 685
—, —, cracking, 136
—, —, hydration of ethylene, 291
—, —, oxidation of paraffin wax, 971
—, —, reaction of ethylene oxide and alcohols, 558
—, —, — oxidized paraffin and pentaerythritol, 1055
—, demulsifying agent, 1111, 1112
—, desulphurizing agent, 489
—, effect on naphthenic acid soaps, 1114
—, extraction agent, naphthenic acids, 1105-1107
—, in dechlorination of 1,2,3,4-tetrachlorobutane, 687
—, in determination of naphthenic acids, 1104
—, in drying of isopropyl alcohol, 364
—, in estimation, of sulphur, 1162
—, in formation of keto-alcohols, 433
—, in preparation of asphalt emulsifiers, 1217
—, in preparation of ethylenediamine, 497
—, in refining gasoline, 669, 670
—, in separation of wax acids, 976
—, reaction with benzyl chloride and ethylene glycol, 543
—, — *sec*-butyl alcohol, 407
—, — cyclohexene peroxide, 898
—, — ethyl alcohol, 342
—, — ethylene dibromide, 533
—, — ethylene dihalides and carbon dioxide, 532
—, — ethylene halohydrins and carbon dioxide, 532
—, — ethyl hypochlorite, 551
—, — olefin halohydrins, 588
—, — polypropene sulphone, 618
—, — sulphur, 828
—, sweetening agent, 475, 477
Sodium hypochlorite, in diisobutylene oxidation, 895
—, reaction with mercaptans, 470
—, — monovinylacetylene, 687
Sodium hypoiodide, reaction with acetylene, 711
Sodium iodide, reaction with triethanolamine, 572
Sodium isopropylxanthate, utilization of, 378
Sodium lauryl sulphate, as detergent, 1084
—, in fireproofing, 1086
—, in de-inking agents, 1086
Sodium mahogany sulphonate, use in grease, 1079
Sodium metaphosphate, catalyst, hydration of ethylene, 287
Sodium metasilicate, emulsifying agent for asphalts, 1217
Sodium methoxide, catalyst, reaction of mercaptans and olefin oxides, 472
—, reaction with difuroyl peroxide, 1152
—, — chlorocyclohexane, 768
Sodium naphthenate, catalyst, oxidation of petroleum, 964
—, uses of, 1113, 1114
Sodium naphtholate, reaction with ethylene dichloride, 500
—, — glycols, 543
Sodium nitrate, in heat-transfer, 861, 862
Sodium nitrite, reaction with acetic acid and β-phellandrene, 620
Sodium nitroprusside, for hydrogen sulphide detection, 466
—, in estimation, of alkyl sulphides, 1159
—, — thiophenol, 1159, 1160
—, reaction with asphaltogenic acids, 1195
Sodium oleate, catalyst, hydrolysis of amyl chloride, 801
—, detergent properties of, 1084
—, in hydrolysis of chlorobenzene, 783
—, surface tension of, 1065, 1066
Sodium oleyl sulphate, as detergent, 1084
Sodium oxide, extraction agent, naphthenic acids, 1105
Sodium palmitate, catalyst, oxidation of petroleum, 964
Sodium peroxide, in estimation of sulphur, 1161, 1162
—, oxidizing agent, for cracked hydrocarbons, 490
—, sweetening agent, 476, 478
Sodium persulphate, oxidizing agent for cracked hydrocarbons, 490
Sodium phenolate, reaction with carbon monoxide and alcohols, 957
—, — chlorobenzene and phenol, 784, 785
—, — ethylene dichloride, 825
—, — naphthenic esters and acids, 1120
Sodium phenyl, reaction with ethylene oxide, 563
Sodium phosphate, effect on asphalt emulsions, 1216
Sodium plumbite, in ozonization of gasoline, 1045
—, in purification of isopropyl alcohol, 365
—, reaction with ethyl iodide, 829
—, — mercaptans, 397, 408, 474, 475
—, sweetening agent, 457, 475, 476, 926
Sodium polysulphide, reaction with ethylene and sulphur chloride, 618, 619
—, — ethylene dichloride, 499, 828
—, sodium thiosulphate from, 465
—, sweetening agent, 477
Sodium pyrosulphate, catalyst, hydration of ethylene, 288
Sodium silicate, catalyst, hydration of acetylene, 714
—, in asphalt emulsions, 1216, 1220
—, inhibitor, dehydration of alcohols, 420
Sodium stannate, in fireproofing agents, 1086
Sodium stearate, detergent properties of, 1084
—, in hydrolysis of chlorobenzene, 783
—, in lubricating oils, 1114
—, reaction with ethylene dichloride, 499
Sodium sulphate, confining agent in gas analysis, 1124
—, effect on naphthenic acid soaps, 1114
—, in cleaning agents, 1112
Sodium sulphide, catalyst, ripening of alkali cellulose, 464
—, in insecticides, 1060
—, reaction with chlorobenzene, 785
—, — ethylene dichloride, 499
—, — ethyl iodide, 819
—, sodium thiosulphate from, 464-466
Sodium sulphite, reaction with benzal chloride, 794
—, sodium thiosulphate from, 465

Sodium sulphonates, in demulsifying agents, 1075
—, in detergents, 1069, 1073
—, in dust fixatives, 1079
—, in oxidation of aromatics, 953
—, surface tension of, 1065-1067
Sodium thiocyanate, reaction with dodecyl chloride, 822
Sodium thiosulphate, from sodium sulphides, 464-466
—, from spent doctor solution, 476
—, in estimation of acetone, 424
—, — gum, 912
—, — sulphur, 1162
—, reaction with ethylene chloride, 829
Sodium triphenylmethyl, catalyst, polymerization of butadiene, 651
Sodium vanadate, inhibitor, corrosion of steel, 574
Sodium zincate, in ozonization of gasoline, 1045
Softening agents, ethylene glycol ethers in, 558
—, from paraffin wax, 1054
—, naphthenic acids in, 1112
—, sulphuric acid esters in, 1112
—, urethans in, 569
—, wax acids in, 975
Softening point, of asphalts, determination of, 1206
Softening point-penetration index, of asphalts, 1208, 1209
Solar oil, oxidation of, 940, 964, 965
Soligen driers, definition of, 1115
Sols, metallic oxides, preparation of, 560
Sorbitol, reaction with ethyl chloride, 826
Soybean oil, cracking of, 136
Soy beans, lecithin from, 728
Sovprene, definition of, 681
Specific dispersion, definition of, 1177
Specific gravity, characterization factor from, 1307, 1309, 1310
—, critical temperature from, 1311, 1312, 1313
—, heat content from, 1327
—, in analysis of gasoline, 144
—, molecular weight from, 1311
—, specific heat from, 1323, 1325
Specific heat, definition of, 1306
—, determination of, 1323, 1325
—, entropy change from, 1277
Specific refraction, determination of, 1177, 1178
Specific parachor, effect on octane number, 1030, 1031
Spectroscope, in estimation of lead tetraethyl in gasoline, 1165
Spindle oil, in detergents, 1073
—, sulphonic acids from, 1074
Spirillum aestuari, decomposition of sulphur compounds by, 490
Spreading coefficient, of asphalts, 1213
Stability number, of lubricants, 933
Standard reference state, definition of, 1278
Squalene, from naphthenic residues, 21
Stannic chloride, catalyst, polymerization of isobutene, 642
—, —, polymerization of styrene, 647
—, —, reaction of acetylene and hydrogen chloride, 716
—, —, — alkylacetylenes and acetyl chloride, 724
—, —, — olefins and acid chlorides, 613
—, reaction with cyclohexane, 1102
—, to determine instability of motor fuel, 911
Stannic oxide, catalyst, methane oxidation, 871
—, —, preparation of cuprene, 704
Stannous chloride, catalyst, chlorination of dioxane, 581
—, nitromethane reduced by, 1094
Stannous phosphate, catalyst, hydrolysis of methyl chloride, 796
Starch, in asphalt emulsions, 1219
—, in gum estimation, 912
—, promoter, reduction of carbon monoxide, 1229, 1230
Stationary flame, theory of, 1006, 1007
Steam, diluent, conversion of propene oxide to allyl alcohol, 586
—, —, oxidation of ethylene, 552, 553, 893
—, —, — kerosene, 860
—, —, — petroleum oils, 1054
Steam, diluent, pyrolysis of hydrocarbons, 93, 156, 178, 190, 192
—, effect on cracking, 127, 128, 131-133
—, — electrical decomposition of methane, 255
—, in activation of carbon, 165, 232
—, in dehydrogenation of menthol, 444
—, in desorption of olefins from charcoal, 164
—, in refining asphaltic residues, 1199
—, pressure-volume-temperature relations of, 1321, 1322
—, reaction with aromatics, 273
—, — butane, 275, 280
—, — carbon monoxide, 871
—, — coke, 1247
—, — coke-oven gas, 1247, 1248
—, — ethyl alcohol, 421
—, — ethyl ether, 421
—, — hydrocarbons, 273, 277, 278, 280
—, — mesityl oxide, 423
—, — methane, 220, 270-273, 276-279, 870, 1246, 1247
—, — natural gas, 276
—, — olefins, 270, 271, 273
—, — olefins and carbon monoxide, 446
—, — petroleum oils, 272, 273
—, — propane, 275, 280
Stearates, catalysts, oxidation of paraffin wax, 971
Stearic acid, bacterial action on, 19
—, catalyst, preparation of ethyl acetate, 304
—, foam-preventing agents from, 1080
—, in candle wax, 543
—, in shaving preparations, 1081
—, reaction with olefins, 588
—, voltolization of, 261
Stearine pitch, in asphalt emulsion preparation, 1216
Steel, catalyst, polymerization of ketene, 441
—, —, pyrolysis of hydrocarbons, 149, 159, 181
Steric hindrance, effect in polymerization, 632
Stilbene, bromination of, 514
—, formation in selenium-acetylene reaction, 720
—, hydrogenation of, 207
—, oxidation of, 895
—, reaction with nitrogen oxides, 621
—, — ozone, 902
Strecker reaction, 819, 820
Strontium boro-phosphate, catalyst, hydration of ethylene, 285
—, —, — propene, 292
Strontium carbonate, catalyst, ketones from ethyl acetate, 423
—, —, polymerization of ethylene oxide, 562
Strontium naphthenates, in inks, 1117
Strontium nitrate, solubility in isopropyl alcohol, 370
Strontium oxide, catalyst, polymerization of ethylene oxide, 562
—, —, reduction of carbon monoxide, 1240
Strontium phosphate, catalyst, hydration of ethylene, 287
—, —, — propene, 292
Structure, effect on entropy change, 1286, 1288-1293
—, — free energy of formation, 1281, 1284, 1286, 1288
—, — stability of aromatics, 1285
Styrene, effect of lead tetraethyl on, 1022
—, ethylcyclohexane from, 1154
—, from acetylene, 718
—, from α-chloroethylbenzene, 805
—, from cracking gases, 645, 646
—, from ethylbenzene, 96, 156, 159
—, from ethylene and benzene, 645
—, from natural gas, 155, 183
—, from propane, 60, 182
—, from vinylacetylene, 705, 706
—, hydrogenation of, 1154
—, mechanism of formation, 156
—, 2 phenyl-1,3-propanediol from, 625
—, polymerization of, 647, 648, 805
—, reaction with aniline hydrochloride, 614
—, — formaldehyde, 625
—, — hydrogen bromide, 318
—, — hydrogen chloride, 311

Styrene, reaction with phenol, 606
—, — toluidine, 614
β-Styrylacrylic acid anhydride, from ketene-cinnamic aldehyde reaction, 439
Submerged combustion, 1061
Succinic acid, catalyst, hydrogenation of olefins, 900
—, from acetylene hydrocarbons, 904
—, from cyclopentane, 876
—, from dibromocyclobutane, 763
—, from maleic acid, 945
—, from paraffin wax, 971
—, solubility of, 959
Succinic anhydride, as antioxidant, 941
—, reaction with thionyl chloride, 945
Succinimide, antioxidant, cracked hydrocarbons, 915
Succinyl peroxide, catalyst, hydrogenation of olefins, 900
Sucrose, 2,3-butene glycol from, 547
Sulphate-bearing waters, reduction by oils, 48
Sulphates, as demulsifying agents, 1085, 1086
—, as detergents, 1073, 1074, 1082-1086
—, as emulsifying agents, 1085, 1086
—, as wetting agents, 1085, 1086
—, from aliphatic acids, 1086
—, from coconut oils, 1084
—, from paraffin wax, 1086
—, in de-inking paper, 1086
—, in shaving preparations, 1081
—, metallic, hydration catalysts, 288
Sulphinic esters, from ethylene, 617
Sulphites, reaction with olefins, 616
Sulphoaromatic stearic acids, catalysts, absorption of propene by sulphuric acid, 358
Sulphobutyric acid, preparation of, 819
β-sulphoethylsulphones, from vinyl sulphones, 618
Sulphonal, preparation from mercaptol, 822
Sulphonated naphthenic acids, as dyes, 1117, 1118
—, in cleaning agents, 1112, 1118
Sulphonated oil, in brake fluid mixtures, 539
Sulphonates, as detergents, 1082-1086
—, as dust fixatives, 1079
—, as emulsifying agents, 1219
—, as siccatives, 1081
—, as tanning agents, 1078
—, classification, 1065
—, from alkyl halides, 804
—, in fungicides, 1078
—, in insecticides, 1078
—, in medicinal preparations, 1080
—, in polishing compositions, 1079
—, in rubber compounding, 1078
—, in shaving preparations, 1081
—, refining with ammonia, 1072, 1073
—, separation of, 1065, 1072, 1073
—, solubility of, 1065
Sulphones, from butadiene homologues, 694-696
—, from olefins, 616, 617
—, from thioethers, 479, 480
Sulphonic acids, as adsorbents, 1080
—, as demulsifying agents, 1074, 1075, 1116
—, as detergents, 1073, 1074
—, as emulsifying agents, 1074, 1075
—, as hydrolyzing agents, 1069
—, as insecticides, 1077, 1078
—, as wetting agents, 1075-1077
—, catalysts, cracking, 114
—, —, dehydration of hydroxy-acids, 968
—, —, esterification of alcohols, 1080, 1081
—, —, reaction of isopropyl alcohol and acetic acid, 376
—, — reaction of propene and sulphuric acid, 358
—, effect of naphthenic acids on, 1069
—, estimation of, 1065
—, from aromatics, 1065
—, from cracked distillates, 1075, 1076
—, from halogenated hydrocarbons, 819, 820
—, from mineral oils, 1074, 1076
—, from olefins, 616
—, from petrolatum, 1069
—, from petroleum distillates, 1069, 1076
—, from shale-oil tar, 1069
—, from sulphurated paraffins, 1083
—, from sulphur dioxide extract, 1076
Sulphonic acids, from thiosulphates, 1083
—, hydrolysis of, 1081
—, in coagulation of carbon, 1081
—, in refining gasoline, 670
—, in treating textiles, 1075-1077
—, properties of, 1064-1068
—, reaction with aldehydes, 1081
—, — aromatic amines, 1068
—, — benzotrichloride, 794
—, — ferric salts, 1065
—, — mercaptans, 472
—, — olefins, 393
—, resins from, 1081
—, separation of, 1065, 1070-1073
Sulphonyl chloride, promoter, bromination of benzene, 790, 791
—, reaction with *o*-dichlorobenzene, 782
Sulphoricinoleic acid, catalyst, sulphation of ethylene, 323
—, —, sulphation of propene, 358
Sulphovinic acid, formation of, 320
Sulphoxides, from thioethers, 479, 480
Sulphur, as heat-transfer medium, 861
—, catalyst, amines from acetone, 428
—, —, bromination of benzene, 790, 791
—, —, chlorination of toluene, 793
—, —, pyrolysis of benzene, 192
—, —, — paraffins, 158
—, colloidal, preparation of, 467, 468
—, corrosive action of, 466
—, effect on catalysts in Kogasin synthesis, 1236
—, — color stability, 455
—, — light stability, 924
—, — pyrolysis of methane, 54
—, estimation of, 1127, 1128, 1156, 1157, 1160-1163
—, from hydrogen sulphide, 460, 461
—, in fungicides, 1078
—, inhibitor, polymerization of chloroprene, 681
—, in insecticides, 1114
—, in lubricants, 469, 486, 1116
—, in petroleum, 454
—, mercaptans from, 1157
—, reaction with acetonaphthone, 469
—, — acetylene, 467, 485, 720
—, — asphalt oil, 467
—, — benzene, 468
—, — benzophenone, 468
—, — carbon tetrachloride, 469
—, — cracked distillates, 467
—, — hydrocarbon oils, 467, 468
—, — hydrogen, 1157
—, — mercaptans, 470
—, — mercury, 1156
—, — potassamide, 469
—, — saturates, 455, 456, 1102
—, — unsaturates, 455, 456, 467, 468
—, removal by alkalies, 115, 489, 1249
—, — alkali polysulphides, 467
—, — brass, 397
—, — cobalt oxide, 397
—, — dichloroethane, 745
—, — halogenation, 490
—, — hydrogenation, 115, 964, 1248, 1249
—, — iron oxide, 1248, 1249
—, — iron sulphide, 397
—, — metallic compounds, 488, 489
—, — oxidation, 489, 490, 964, 1043, 1044
—, — phenol, 134
Sulphurated paraffins, sulphonic acids from, 1083
Sulphur chloride, catalyst, chlorination of ethylene, 495
—, —, — propene, 507
—, in estimation of lead tetraethyl, 1165
—, reaction with diolefins and oxygen, 696
—, — ethylene and sodium polysulphide, 618, 619
—, — mercaptans, 481
—, — olefins, 618, 619
—, — saturated hydrocarbons, 1102
—, refining agent, gasoline, 929
Sulphur compounds, autoxidation of, 905
—, corrosion by, 456
—, decomposition by bacteria, 490
—, effect of distillation on, 11

Sulphur compounds, effect on asphaltene formation, 1190
—, — color stability, 454-456
—, — lead susceptibility, 456
—, — light stability, 924
—, in crude oils, 11, 12, 17
—, in gases, estimation of, 1125
—, inhibitors, polymerization of chloroprene, 681
Sulphur content, of commercial propane, 25
—, of petroleum, 454
—, reduced during aquolysis, 133
Sulphur dichloride, carbon tetrachloride from, 730
Sulphur dioxide, effect on ethylene polymerization, 639
—, estimation of, 1125
—, extraction agent, acetylene, 169
—, — aromatics, 30, 35, 36
—, — naphthenic acids, 1107
—, — nitrogen bases, 832, 838
—, — olefins, 163, 213
—, —, petroleum distillates, 41, 42, 925, 1070, 1076, 1205
—, —, petroleum oxidation products, 862, 977
—, —, phenols, 1107
—, —, polymerized hydrocarbons, 397
—, in desulphurizing oils, 1044
—, in insecticides, 1077
—, in separation of butenes and butanes, 1141
—, inhibitor, deposition of carbon, 192
—, oxidation of sodium hydrosulphide with, 465
—, — sodium sulphide with, 465
—, reaction with allyl ethers, 616
—, — cycloolefins, 616-618
—, — diolefins, 176, 694-696
—, — hydrogen sulphide, 457, 459
—, — olefins, 616-618
—, reduction to hydrogen sulphide, 128
Sulphur trioxide, as sulphonating agent, 1069
—, reaction with ethylene dichloride, 517, 518
Sulphuric acid, ammonium sulphate from, 320
—, catalyst, acetylation of cellulose, 496
—, —, alkylation of alcohols, 606, 607
—, —, — aromatics, 591-593, 598
—, —, — phenols, 603, 604
—, —, condensation of dichlorobutenes, 685
—, —, cracking, 114
—, —, dehydration of alcohols, 331, 410
—, —, electrolytic oxidation of cyclohexanone, 451
—, —, esterification of *ter*-alcohols, 409, 412
—, —, — ethylene glycol, 541
—, —, — olefins, 304, 307, 314
—, —, — phthalic anhydride, 541
—, —, ethers from alcohols, 413
—, —, hydration of acetylene, 712
—, —, — butenes, 294
—, —, — ether, 332-334
—, —, — ethylene, 282-284, 1302, 1303
—, —, — ethylene oxide, 557
—, —, — olefins, 297, 410
—, —, — propene, 291
—, —, hydrolysis of isopropyl sulphates, 363
—, —, nitration of acetic anhydride, 1090
—, —, oxidation of asphalts, 1205
—, —, polymerization of aldehydes, 579
—, —, — diolefins, 171
—, —, — olefins, 255, 634, 635, 642, 672
—, —, — styrene, 647
—, —, reaction of acetic acid and cyclohexanol, 405
—, —, — acetic acid and diisopropyl ether, 377
—, —, — acetic acid and isopropyl alcohol, 376
—, —, — alcohols and acetylene, 715
—, —, — alcohols and alkene oxides, 558, 589
—, —, — *sec*-alcohols and aromatics, 382, 401, 409, 411, 412
—, —, — *ter*-alcohols and phenols, 409, 412, 416
—, —, — butyl alcohol and phthalic anhydride, 501
—, —, — ethylene glycol and olefins, 544
—, —, — glycols and formaldehyde, 543
—, —, — isopropyl alcohol with *p*-nitrotoluene, 382
—, —, — ketene and phenol, 438
—, —, — monoalkyl ethers and monohydric alcohols, 544
—, desulphurizing agent, 488
Sulphuric acid, extraction agent, aromatics, 30, 1081, 1149, 1150
—, —, naphthenic acids, 1107
—, —, nitrogen bases, 832, 833
—, —, olefins, 161, 389, 390, 1135
—, from hydrogen sulphide, 464
—, in analysis of gasoline, 30, 31
—, in bleaching montan wax, 1057
—, in detecting *ter*-butanol, in isopropyl alcohol, 365
—, in estimation of alcohol in blended fuels, 1185
—, — lead in greases, 1165
—, — lead tetraethyl in gasoline, 1165, 1166
—, — olefins, 1141, 1142, 1151, 1154
—, in extracting bromine from sea water, 504
—, in oxidation of isopropyl ethylene glycol, 548
—, reaction with alcohols, 1085
—, — *sec*-alcohols, 400, 406
—, — *ter*-alcohols, 410, 411, 417
—, — aliphatics, 1082
—, — aromatics, 1154
—, — asphaltenes, 1191
—, — benzene, 669
—, — butenes, 308, 309, 385-387, 389-392
—, — calcium butyrate, 443
—, — carbenes, 1193
—, — carboids, 1193, 1194
—, — ceresins, 39
—, — chloroethanes, 746, 829, 830
—, — cracked distillates, 1075, 1076
—, — cracking gases, 359
—, — cycloaliphatics, 1082
—, — cyclohexene, 392
—, — cyclohexene peroxide, 898
—, — diethanolamine, 583
—, — diethylene glycol and nitric acid, 546
—, — di-β-hydroxypropylamine, 585
—, — ethers, 378, 379
—, — ethyl alcohol, 343
—, — ethylene, 161, 298, 319-325, 1081, 1082
—, — glycols and naphthol, 543
—, — hexenes, 308, 388, 389
—, — hydrocarbon oils, 134
—, — isobutene, 308, 385, 386, 391
—, — isonitrosoethyl methyl ketone, 452
—, — isopropylethylene, 309
—, — methylethylpinacone, 678
—, — naphthalene, 409
—, — naphthenic acids, 1117, 1118
—, — naphthenic alcohols, 1120
—, — nitroethane, 1096
—, — nitrolic acids, 1094
—, — nitromethane, 1096
—, — octenes, 1083
—, — pentenes, 308, 310, 318, 387, 388, 391
—, — polyglycols, 545
—, — propene, 161, 305, 306, 323, 356, 357, 359, 362, 363, 392
—, — shale-oil tar, 1069
—, — trimethylethylene, 308, 391
—, refining agent, asphalts, 1192
—, —, cracked distillates, 214
—, —, diaryl hydrocarbons, 193
—, —, ether, 336
—, —, green oil, 242
—, —, isopropyl alcohol, 365
—, —, naphthenic acids, 1110
—, —, petroleum distillates, 35, 263, 668, 669, 1069, 1070
—, solubilities of ethers in, 378, 379
Sulphuric acid esters, catalyst, absorption of olefins, 392
—, formation of, 298
—, reaction with naphthenic acids, 1112
—, utilization, 1112
Sulphurous acid, reaction with olefins, 616
Sulphuryl chloride, catalyst, condensation of cyclohexane, 205
—, —, nitration of acetic anhydride, 1090
—, —, reaction of methylene chloride and formaldehyde, 728
—, reaction with cyclohexane, 1102
Sunlight, inhibitor, polymerization of acetylene, 703
—, to accelerate gasoline oxidation, 909
—, use in refining gasoline, 669

Surface tension, determination of, 1180
Susceptibility factor, of asphalt, 1210
Sweetening, defined, 474
—, with alkalies, 477
—, with bauxite, 478, 488
—, with chromite ore, 479
—, with chromium-lead ore, 479
—, with copper oxide, 667
—, with copper salts, 476, 477
—, with fuller's earth, 479
—, with hypochlorites, 478
—, with lead compounds, 475, 476
—, with peroxides, 476, 478
Synthetic index, in knock rating, 1027
Synthin, from carbon monoxide and hydrogen, 1223
Synthol, from carbon monoxide and hydrogen, 1223
—, olefins from, 1252

T

Tannic acid, in asphalt emulsions, 1219
Tanning agents, ammonium sulphate in, 1078
—, sulphonates in, 1078
Tantalum, promoter, oxidation of toluene, 949
Tantalum oxide, catalyst, oxidation of aromatics, 942
Tantalum pentachloride, catalyst, alkylation of aromatics, 596
Tar formation, during aquolization, 131
—, pyrolysis of *n*-hexane, 71
Tar oils, lampblack from, 242
Tar stripper, function of, 120
Tars, acetylene from, 254
—, aquolysis of, 132
—, chlorination of, 756
—, electrical cracking of, 131
—, extraction with choloroform, 729
—, inhibitors, gum formation in gasoline, 914
—, monomethyl naphthalene isomers in, 40
—, motor fuel from, 1046
—, viscosity of, 1174
Tartaric acid, discolorizing agent, 958
—, from fumaric acid, 547
—, from furfuraldehyde, 945
—, from maleic acid, 547
—, inhibitor, alligatoring effect of paint, 576
Tellurium, catalyst, bromination of benzene, 790, 791
—, — dehydrogenation of paraffins, 158
—, use in lubricants, 469
Tellurium oxide, catalyst, oxidation of aromatics, 942
—, —, oxidation of olefins, 553
Tellurium phosphate, catalyst, hydration of ethylene, 287
Telluroformaldehyde, polymerization of, 51
—, stability of, 53
Tellurophene, formation of, 720
Telsa discharge, action on aromatics, 260
Temperature, effect on combustion of hydrocarbons, 1005
—, — cracking, 105, 139, 143, 150, 152, 188
—, — heat content change, 1293
—, — ignition of safety fuel, 1002
—, — inflammability limits, 980-982
—, — knock rating, 1030
—, — polymerization of olefins, 664
—, effect on free energy change, 1293-1295
—, —, alkylation of isobutane, 1301
—, —, hydration of ethylene, 1302, 1303
—, —, hydrogenation of benzene, 1298, 1299
—, —, hydrogenation of olefins, 1299, 1300
—, —, isomerization of cyclohexane, 1301, 1302
—, —, polymerization of isobutene, 1300
—, —, reduction of carbon monoxide, 1304, 1305
—, effect on free energy of formation of acetaldehyde, 1304
—, — acetylenes, 1294
—, — alcohols, 1294, 1295
—, — carbon monoxide, 1304
—, — naphthenes, 1294
—, — olefins, 1294, 1295
Temperature, effect on free energy of formation of paraffins, 1294, 1295
—, — water, 1304
—, heat content from, 1327
—, relation to free energy change, 1275, 1276
—, specific heat from, 1323, 1325
Temperature-entropy relations, 1335-1341
Temperature-pressure-enthalpy relations, 1332-1335
Temperature-volume-pressure data, correlation, 1320-1322
Terpenes, as antiknocks, 1017
—, by diene reaction, 688
—, from carbon monoxide and hydrogen, 1244
—, from coniferous wood, 46
Terephthalyl chloride, reaction with isopropyl hydroperoxide, 382
Terpineol, as antiknock, 1017
—, as blending agent, 1035
—, reaction with formaldehyde, 624
Tertiary alcohols, condensation with phenols, 416
—, dehydration of, 410
—, esters of, 412
—, ethers from, 413
—, from ketones, 452
—, oxidation of, 410
—, reaction with aromatics, 411
—, — phenols, 412
Tertiary alkyl hypohalites, preparation of, 418
Tertiary olefins, from tertiary alcohols, 410
—, reaction with hydrogen halides, 310
—, — ethylene glycol, 544
—, separation from secondary olefins, 314
Tetra-alkylphenols, antioxidants for gasoline, 916
Tetrabromobenzene, from benzene, 790, 791
Tetrabromocyclobutane, preparation of, 763
Tetrabromocyclohexane, preparation of, 770
Tetrabromocyclohexanone, preparation of, 770
Tetrabromoethane, preparation of, 747
Tetrabromopentane, from amylene, 513
1,2,4,5-Tetrachlorobenzene from dichlorobenzenes, 781
Tetrachlorobutadiene, from butadiene, 685
Tetrachlorobutane, preparation of, 811
—, 2,3-dichlorobutadiene from, 686, 687
Tetrachlorocyclopentane, preparation of, 763
Tetrachloroethane, as cooling medium, 746
—, dechlorination of, 805
—, from carbon tetrachloride, 731
—, in cleaning fluids, 746
—, in insecticides, 747
—, in manufacture of films, 746
—, reaction with sulphuric acid, 746, 829
—, stabilization of, 743
Tetrachloroethylene, purification of, 745
Tetrachloromethane, *see* Carbon tetrachloride
Tetrachloropentane, formation of, 511
Tetrachloropyrene, oxidation of, 956
Tetracosene, from isobutene, 643
Tetradecane, cracking of, 100, 101, 1297
—, —, free energy change, 1297
—, from di-*n*-heptyl mercury, 71
Tetradecene, in kerosene, 145
Tetraethylene glycol, from ethylene oxide, 557
Tetraethanol ammonium hydroxide, preparation of, 572
Tetraethyl lead, *see* Lead tetraethyl
Tetrahexacontane, synthesis of, 40
Tetrahydrobenzene, from cyclohexane, 93
Tetrahydrofurfuryl alcohol, as extraction agent, 44
Tetrahydronaphthalene, corrosion inhibitor, 477
—, in dewaxing lubricants, 433
—, in motor fuel, 1039
—, reaction with chlorinated Kogasin, 1253, 1254
—, — ethylene, 594
Tetrahydro-α-naphthol, from tetralin peroxide, 906
1,2,4,5-Tetraisopropylbenzene, synthesis of, 382
Tetraisopropyl hydroferrocyanate, antiknock, 1018
Tetralin, absorbent for butadiene, 174
—, autoxidation of, 905, 906
—, ethylation of, 209, 210
—, preparation of, 649
Tetralin peroxide, as antiknock, 1017, 1018
—, formation of, 905
—, reaction with iron carbonyl, 906

Tetralin peroxide, reaction with potassium permanganate, 905
—, reduction of, 906
Tetramethylbenzene, from petroleum, 35
1,2,3,4-Tetramethyl-1,3-butadiene, from methylethylpinacone, 678
Tetramethylethylene, dinitrate from, 621, 622
—, dinitrite from, 621
—, from di-*ter*-butylethylene, 87, 411, 645
—, nitro-nitrate from, 621, 622
—, polymerization of, 643, 645
—, reaction with nitrogen tetroxide, 621
—,1,1,2-trimethyl propanol from, 388
Tetramethylene bromide, reaction with mercaptans, 485
Tetramethylethylene chlorohydrin, preparation of, 520
3,4,5,5-Tetramethylhexene-2, from 1,2-dimethylpropanol-1, 400
Tetramethylmethane, *see* Neopentane
2,2,3,4-Tetramethylpentanol-3, dehydration of, 411
2,2,4,4-Tetramethylpentanol-3, dehydration of, 401
1,2,3,3-Tetramethylpentene-2, synthesis of, 411
2,3,4,4-Tetramethylpentene-2, synthesis of, 411
Tetranitromethane, synthesis of, 1090
Tetranitromethylaniline, as antiknock, 1017
Tetrasulphides, preparation of, 481
—, use in Diesel fuels, 486
Tetryl, purification of, 496
T-gas, definition of, 556
Thallium, catalyst, chlorination of ethane, 741
Thallium alkyls, as antiknocks, 1018
Thallium aryls, as antiknocks, 1018
Thallium halides, catalyst, dehydrogenation of hydrocarbons, 158
Thallium oxide, catalyst, oxidation of aromatics, 942
—, catalyst, oxidation of pinene, 905
Thermatomic process, for carbon black, 219, 220
Thermax carbon black, 235
Thermodynamic variables, engineering, definitions of, 1306, 1307
—, units of, 1272
Thermodynamics, application to petroleum technology, 99
—, limitations of, 1276, 1295-1297
—, nomenclature, 1272, 1273
—, of cracking, 99
—, third law of, 1277
Thianthrene, from benzene, 468
Thioacetaldehyde, from acetylene, 720
Thioalcohols, reaction with ketene, 438
Thiocarbamides, for stabilizing carbon tetrachloride, 730, 731
Thiocarbonates, preparation of, 487
Thiocresol, reaction with acetylene, 473
—, — divinylacetylene, 709
—, — formaldehyde, 473, 474
Thiocyanates, extraction agents, 44
Thiocyanogen, preparation of, 629
—, — butadiene, 698
—, — olefins, 629, 1152, 1153
Thiodiarylamines, antioxidants for gasoline, 918
Thiodiethylene glycol, formation of, 564
Thioethers, boiling points of, 479
—, effect on lead susceptibility, 1031
—, from mercaptans, 472, 473, 479
—, heats of vaporization, 479
—, in petroleum, 454
—, oxidation of, 479, 480
—, reaction with ammonia and sulphur, 481
—, — mercuric chloride, 479
—, solvents for rubber, 486
Thioethylene glycol, from ethylene oxide, 563
Thioindigo, preparation of, 469
Thicnaphthene, from acetylene, 720
Thionylaniline, reaction with mercaptans, 481
Thionyl chloride, reaction with alcohols, 413
—, — acid anhydrides, 945
—, — cyclohexane, 1102
—, — 1,4-cyclohexanediol, 766
—, — cyclohexanol, 766
—, — ethanolamines, 570
—, — ethylene chlorohydrin, 525
—, — hydroxy thioethers, 526
Thionyl chloride, reaction with mercaptans, 481
—, — trichloroacetyl glycol, 541
Thiophanes, dehydrogenation of, 484
—, isolation of, 484
—, oxidation of, 1043
—, preparation of, 484
Thiophene, from acetylene, 467, 720
—, from cracked distillates and sulphur, 467
—, hydrogenation of, 484, 485
—, in petroleum, 454, 483
—, pyrolysis of, 483
—, reaction with acetyle chloride, 611
—, — acetyl iodide, 611
—, — hypochlorous acid, 490
—, — mercuric chloride, 483
—, removal by carbon monoxide, 483
—, — oxidation, 1043
Thiophenol, estimation with sodium nitroprusside, 1159, 1160
—, from chlorobenzene, 785
—, separation from phenols, 476
Thiophthene, preparation of, 467, 484, 485, 720
Thiophthene, properties of, 484
Thiosulphates, oxidation of, 1083
—, reaction with alkyl halides, 829
—, sulphonic acids from, 1083
Thiourea, in fungicides, 569
—, in synthetic resins, 890
—, reaction with amines, 587
—, — ethylene oxide, 564
Thiuram disulphide, inhibitor, polymerization of chloroprene, 681
Thoria, catalyst, decomposition of ether, 335
—, —, dehydration of alcohols, 399
—, —, dehydration of glycol ethers, 174
—, —, dehydrogenation of paraffins, 159
—, —, esterification of alcohol, 339
—, —, ether from ethyl alcohol, 331
—, —, hydration of ethylene, 289
—, —, isomerization of propene oxide, 586
—, —, methane-steam reaction, 272, 278
—, —, oxidation of ethylene, 553
—, —, pyrolysis of olefins, 190
—, —, — oxygenated hydrocarbons, 340
—, —, reduction of carbon monoxide, 1228, 1235, 1236, 1237, 1240
Thoria aerogel, catalyst, pyrolysis of propionic acid, 446
Thorium, catalyst, pyrolysis of acetals, 715
—, promoter, oxidation of methyl alcohol, 878, 879
—, —, reduction of carbon monoxide, 1228, 1229, 1230, 1232, 1236, 1249, 1250
Thorium compounds, catalysts, acetylene-ammonia reaction, 719
Thorium dioxide, catalyst, cracking of petroleum, 111
—, —, reduction of carbon monoxide, 1228, 1229
Thorium oxide, catalyst, dechlorination of propyl chloride, 805
—, —, decomposition of acids to ketones, 443, 446
—, —, hydration of acetylene, 714
—, —, hydration of glycols, 548
—, —, hydrogen-carbon monoxide reaction, 661
—, —, hydrolysis of chlorobenzene, 782
—, —, methane-steam reaction, 270, 278, 279
—, —, nitration of paraffins, 1091
—, —, oxidation of aromatics, 942
—, —, oxidation of hydrocarbons, 850, 851
—, —, — methyl alcohol, 878
—, —, production of biphenyl, 192
—, —, pyrolysis of isobutyl bromide, 806
—, —, — mesityl oxide, 423
—, —, reaction of amines and alcohols, 614
Thorium nitrate, promoter, reduction of carbon monoxide, 1232
Thymol, reaction with isoamylene, 606
Thymol monosulphide, as antioxidant, 941
Time factor, in cracking, 105, 139
Time-temperature index, use of, 105, 106
Tin, alloys of, in cracking, 113
Tin, antioxidant, for insulating oils, 939
—, catalyst, oxidation of ethylene, 552
—, —, — lubricants, 933
—, —, — naphthenes, 939, 940
—, —, — paraffins, 660

Tin, catalyst, polymerization of olefins, 665
—, —, pyrolysis of hydrocarbons, 160, 189, 191
—, effect on sludge formation, 939
—, use in refining gasoline, 668
Tin chloride, catalyst, chlorination of ethylene, 495
—, —, — propene, 507
—, —, ether from ethyl alcohol, 331
—, desulphurizing agent, 488
Tin dioxide, catalyst, decomposition of natural gas, 227
Tin halides, catalyst, dehydrogenation of hydrocarbons, 158
Tin iodide, catalyst, acetone-amine reaction, 429
Tin naphthenate, as antioxidant, 1116
Tin oleate, as antioxidant, 938
Tin oxide, catalyst, acetone from ethyl alcohol, 422
—, —, acetylene-steam reaction, 714
—, —, oxidation of aromatics, 942
—, —, — methyl alcohol, 878
—, effect on ignition temperatures, 1000
—, for hydrogen sulphide removal, 458
—, for refining gasoline, 929
Tin phosphate, catalyst, hydration of ethylene, 287
—, —, hydrolysis of methyl chloride, 727
—, —, — methylene chloride, 728
Tin ricinoleate, antioxidant for lubricants, 933
Tin tetrachloride, catalyst, polymerization of olefins, 195
—, —, preparation of gasoline, 195
Tin tetraethyl, antioxidant for lubricants, 933
Tin tetraphenyl, antioxidant for lubricants, 933, 938
Titania, catalyst, esterification of alcohol, 339
—, —, pyrolysis of propene oxide, 586
Titanic acid, promoter, pyrolysis of alcohol, 351
Titanium, use in alloys, 134
Titanium carbide, catalyst, oxidation of naphthalene, 946
Titanium chloride, catalyst, polymerization of olefins, 636, 665
—, —, preparation of gasoline, 203
—, desulphurizing agent, 488
Titanium dioxide, catalyst, cracking of petroleum, 111
Titanium halides, catalyst, dehydrogenation of hydrocarbons, 158
—, —, reaction of olefins and carbon monoxide, 625, 626
Titanium naphthenate, as wetting agent, 1117
Titanium oxide, catalyst, hydration of acetylene, 714
—, —, hydrolysis of chlorobenzene, 782
—, —, methane-steam reaction, 279
—, —, methyl alcohol-carbon monoxide reaction, 1050
—, —, oxidation of hydrogen sulphide, 460
—, —, — aromatics, 942
—, —, preparation of monovinyl acetylene, 705
—, —, pyrolysis of methane, 228
Titanium phosphate, catalyst, hydration of ethylene, 287
Titanium tetrachloride, catalyst, alkylation of aromatics, 596
—, —, polymerization of isobutene, 204, 210, 642
—, in refrigerants, 738
Toluene, acetylene from, 260
—, action of aluminum chloride on, 208
—, — silent discharge on, 260
—, — Tesla discharge on, 260
—, as antiknock, 1017
—, as blending agent, 1035
—, bromination of, 794, 795
—, by polymerization of cracking gas, 646
—, by pyrolysis of alcohol, 173, 177
—, — cylinder oil, 137
—, — gas oil, 178
—, — gasoline, 136
—, — kerosene, 137, 144
—, — natural gas, 183
—, chlorination of, 793, 794
—, coloring matter prepared from, 215
—, detection in alcohol, 354
—, for estimation of water in oils, 1168
—, for extraction of olefins, 163
Toluene, from allyltoluene, 96
—, from benzene, 206
—, from carbon monoxide and hydrogen, 1243
—, from cycloheptane, 94
—, from 2,6-dimethylanthracene, 96
—, from ethylbenzene, 96
—, from ethylcyclohexane, 93
—, from ethylene, 77, 186
—, from *n*-heptane, 73
—, from isobutene, 85
—, from pinene, 88
—, from propane, 60, 182
—, from xylene, 96, 208
—, hydrogenation of, 347
—, in dehydration of isopropyl alcohol, 364
—, inflammability limits of, 980, 981
—, in gasoline, 34, 35, 144, 196
—, in motor fuel, 1039
—, molal entropy, 1290
—, nitration of, 954, 1091
—, oxidation of, 843, 942-944, 947-950, 953, 954
—, reaction with acetic acid, 448
—, — acetylene, 718
—, — amyl alcohols, 411
—, — *sec*-butyl alcohol, 402
—, — *ter*-butyl alcohol, 411
—, — chlorinated Kogasin, 1253, 1254
—, — isopropyl alcohol, 382, 401, 402
—, — nitrosyl chloride, 794
—, — propene, 594, 596
—, toluquinone from, 953
Toluene sulphonamide, alkyl derivatives in brake fluids, 542
p-Toluenesulphonic acid, catalyst, dehydration of tertiary alcohols, 410
—, —, hydration of olefins, 297, 410
Toluidine, as antiknock, 1018
m-Toluidine, from *m*-cresol, 788
o-Toluidine, reaction with ethyl chloride, 808
—, — sulphonic acids, 1068
p-Toluidine, reaction with sulphonic acids, [illegible]
—, — styrene, 614
Toluquinone, from toluene, 953
o-Tolyl ammonium chloride, preparation [illegible]8
Tolylenediamines, antioxidants for gas[illegible]7
β-*p*-Tolylethyl alcohol, preparation of [illegible]
p-Tolyl-*β*-sulphoethylsulphone, prepa[illegible]
Tonsil, catalyst, hydrolysis of chlor[illegible]
Top oils, preparation of, 968
Total heat, definition of, 1306
—, of naphtha, 15
—, of pentane, 15
Transformer oil, antioxidants for, 941
—, oxidation of, 963
—, sludge formation in, 940
—, sulphonation of, 1065
Transition reaction, definition of, 56
Triacetin, in brake fluids, 546
—, methane from, 19
Tribromobenzene, from benzene, 791
Tribromopentane, from amylene, 513
Tri-*ter*-butylbenzene, preparation of, 592
Trichloroacetaldehyde, *see* Chloral
Trichloroacetic acid, promoter, alcohol-vinylacetylene reaction, 706
—, —, alkylation of benzene, 596
—, reaction with cyclohexene, 313
—, — ethers, 345
—, — ethylene oxide, 540
—, — isopropyl alcohol, 376
—, — propene, 308
—, — trimethylethylene, 313
Trichloracetyl chloride, reaction with methoxymethanol, 541
Trichloroacetyl glycol, preparation of, 540
—, reaction with acetyl chloride, 541
—, — ammonia, 541
—, — diazomethane, 540
—, — ethyl alcohol, 541
—, — thionyl chloride, 541
—, structure of, 540, 541
Trichloroacetyl glycol methyl ether, preparation of, 541
—, reaction with ethyl alcohol, 541
Trichlorobenzene, in dielectrics, 789

1,2,4-Trichlorobenzene, in lubricating oil, 790
Trichlorobenzyl chloride, reaction with benzene, 816
Trichlorobutane, preparation of, 811
Trichloro-*ter*-butyl alcohol, from chloroisobutene, 522
1,2,3-Trichloro-2-chloromethylbutane, formation of, 513
Trichlorocyclopentane, preparation of, 763
Trichlorocyclopropane, formation of, 761
Trichlorodiphenylmethane, as transformer oil, 816
—, preparation of, 816
Trichloroethane, fluorodichloroethane from, 747
—, from ethylene dichloride, 501
—, from vinyl chloride, 716
Trichloroethylene, action of light on, 710
—, as anesthetic, 711
—, as solvent, 710
—, corrosive action of, 710, 711
—, decaffeination agent, 710
—, detection of, 710
—, for dewaxing oils, 710
—, from acetylene tetrachloride, 710
—, in alcohol distillation, 327, 328
—, in insecticides, 747
—, separation of acids with, 967, 968
—, stabilization of, 328, 710
—, toxicity of, 710
Trichlorofluoromethane, from carbon disulphide, 737
—, from carbon tetrachloride, 734
Trichloromercuriacetaldehyde, formation of, 702
Trichloromethane, *see* Chloroform.
1,2,3-Trichloro-2-methylbutane, formation of, 513
1,2,3-Trichloro-2-methylpropane, hydrolysis of, 797, 798
Trichloropentane, formation of, 511, 512
Trichloropropane, preparation of, 506
—, as cleaning agent, 751
1,1,2-Trichloropropane, from propene dichloride, 508
1,2,3-Trichloropropane, from propene dichloride, 507, 508
Trichlorotrifluorobenzene, as solvent, 792
Trichlorotrifluoroethane, diluent, fluorination of benzene, 792
n-Tridecane, reaction with benzene, 1254
Tridecene, from tetradecane, 100
—, in kerosene, 145
Tridecylxylene, preparation of, 1254
Tri-(2,5-dichlorophenyl) methane, from dichlorobenzene, 729
Triethanolamine, as pour depressant, 577
—, dehydration agent, 538, 578
—, estimation of, 572
—, inhibitor of gum formation, 915
—, miscellaneous uses of, 575-576
—, preparation of, 567
—, reaction with carbon dioxide, 578
—, — fluorochloromethanes, 737
—, — metallic salts, 570-572
—, — trinitrotoluene, 570
—, — wood rosin, 578
—, removal of hydrogen sulphide by; 458, 574, 575
—, use in decarbonizing, 790
—, — electrodeposition of metals, 571
—, — ethylene dichloride-sodium polysulphide reaction, 499
—, — ethylene oxide-benzene reaction, 563
Triethanolamine bicarbonate, for carbon dioxide removal, 574
Triethanolamine hydrochloride, solubility in alcohols, 568
Triethanolamine hydroxyabietate, preparation of, 578
Triethanolamine lactate, uses for, 578
Triethanolamine oleate, in emulsifying agents, 1074, 1217
—, in wetting agents, 1076
Triethanolamine soaps, uses of, 575, 576
Triethylamine, stabilizing agent, 328
Triethylbenzene, from ethylbenzene, 208
Triethyl carbinol, from diethyl ketone, 452
Triethylene glycol, from glycol, 557
Triethylene glycol propionate, in cellulose compositions, 546
Triethylethylene, from isobutene, 85
Triethylmethane, in motor fuel, 501, 1039
—, oxidation of, 876
Triethylolsulphonium hydroxide, preparation of, 564
Trifluorotrichloroethane, preparation of, 735
Trihydroxyethyl sorbite, reaction with isopropyl urea, 587
Triisobutylene, from isobutene, 591, 642
—, reaction with benzene, 592
—, — hydrogen chloride, 311
—, — phenol, 605
Triisopropanolamine, preparation of, 587
Triisopropylbenzene, preparation of, 382
Triisopropyltoluene, preparation of, 382
Trimethylacetic acid, from acetone, 432
—, from *n*-butane-carbon monoxide reaction, 1100
—, from 2-butene, 626
—, *see also* Pivalic acid
Trimethylbenzene, in petroleum, 34, 35
—, molal entropy, 1290
—, *see also* Pseudocumene
2,2,3-Trimethylbutane, molal entropy, 1292, 1293
Trimethylcarbinol, *see also* *ter*-Butyl alcohol
1,1,4-Trimethylcycloheptane, pyrolysis of, 94
1,1,4-Trimethylcycloheptene, dehydrogenation of, 94
—, isophthalic acid from, 94
Trimethylcyclohexane, in petroleum, 34
—, chlorination of, 775, 776
Trimethylene, extraction agent, 44
Trimethylene glycol, reaction with 2,3-dichloro-1,4-dioxane, 549
Trimethylene glycol diacetate, as solvent, 549
Trimethylene mercaptan, reaction with methylene chloride, 485
—, tetramethylene bromide, 485
Trimethylethylene, *ter*-amyl alcohol from, 387, 391
—, *ter*-amyl nitrate from, 623
—, co-polymerization with hexadiene, 216
—, from 2,2,4,4-tetramethylpentanol-3, 401
—, glycols from, 547, 895
—, in gasoline, 144
—, polymers of, 203, 210, 633
—, reaction with chlorine, 513
—, — hydrogen chloride, 310
—, — hydrogen peroxide, 547
—, — nitric acid, 623
—, — nitric acid and amyl nitrite, 621
—, — nitrogen pentoxide, 621
—, — nitrogen tetroxide, 621
—, — sulphuric acid, 308, 391
—, — trichloroacetic acid, 313
—, *see also* Isoamylene and 2-Methyl-2-butene
Trimethylethylene bromide, glycol from, 547
Trimethylethylene chlorohydrin, preparation of, 520
Trimethylethylene glycol, preparation of, 895
3,5,5-Trimethylheptene-2, from 1,2-dimethylpropanol-1, 400
2,2,4-Trimethylhexene-2, preparation of, 411
3,3,5-Trimethylhexene-2, preparation of, 411
2,4,4-Trimethylhexene-3, preparation of, 411
Trimethylmethane, in motor fuel, 501, 1039
2,2,4-Trimethylpentane, action of aluminum chloride on, 199-201
—, formation of, 417
—, isomers, molal entropy of, 1289
—, reaction with benzene, 602, 603
—, — ethylene, 599
—, *see also* Isooctane
2,4,4,-Trimethyl-2-pentene, pyrolysis of, 87
1,1,2-Trimethylpropanol, from tetramethylethylene, 388
Trimethylpyridine, preparation of, 719
2,3,8-Trimethylquinoline, from petroleum, 834
Trinidad asphalt water-white hydrocarbons from, 1187
Trinitrophenol, estimation of aromatics with, 1154, 1155
Trinitrotoluene, reaction with diethanolamine, 570
—, separation from dinitrotoluene, 496

Triphenylamine, preparation of, 787, 810
Triphenyl bismuth, antioxidant for lubricants, 938
Triphenylcarbinol, from triphenylmethane, 957
Triphenylchloromethane, reaction with cyclohexadiene, 694
Triphenylene, from cyclohexanone, 451
Triphenylethane, from stilbene, 207
Triphenylethylene, reaction with ozone, 902
Triphenylmethane, molal entropy, 1289
—, oxidation of, 943, 957
Triphenyl phosphate, antioxidant for gasoline, 917
Triple point, definition of, 743
Tripropanolamine, reaction with cobalt chloride, 587
Trisodium phosphate, catalyst, dehydration of 1,3-butene glycol, 174
—, emulsifier for asphalts, 1217-1219
sym-Trithiane, from formaldehyde, 463
Trouton's law, defined, 479
Tube and Tank process, for cracking, 117
Tungsten, catalyst, hydration of ethylene, 291
—, —, pyrolysis of acetals, 715
—, —, — paraffins, 160, 169, 189
—, —, reaction of butene with sulphuric acid, 387
—, in cracking, 114
—, in preparation of amines, 428
—, promoter, oxidation of methyl alcohol, 879
—, —, — toluene, 949
Tungsten carbonate, catalyst, oxidation of methane, 881
Tungsten compounds, catalyst, acetylene-ammonia reaction, 719
—, —, olefin-carbon monoxide reaction, 626
Tungsten halides, catalyst, dehydrogenation of hydrocarbons, 158
Tungsten oxide, catalyst, aromatics from paraffins, 189
—, —, cracking of ethylbenzene, 159
—, —, cracking of heavy oils, 115
—, —, dehydrogenation of paraffins, 158
—, —, hydration of acetylene, 712
—, —, hydrolysis of chlorobenzene, 782
—, —, methane-steam reaction, 279
—, —, methanol-carbon monoxide reaction, 1050
—, —, nitration of toluene, 954
—, —, oxidation of aromatics, 942, 945
—, —, — hydrogen sulphide, 460
—, —, — methane, 881
—, —, pyrolysis of benzene, 192
—, —, — methane, 228
—, —, reaction of amines and alcohols, 614
—, —, reduction of carbon monoxide, 1228
Tungsten salts, catalyst, oxidation of olefins, 894
—, —, propene absorption by sulphuric acid, 357
Tungstic acid, catalyst, hydration of acetylene, 712
—, —, — ethylene, 288-291
—, —, methanol-carbon monoxide reaction, 1050
Tungstic acid salts, catalyst, hydration of ethylene, 288
Tungstic sulphide, catalyst, hydration of acetylene, 712
Turkey-red oil, promoter, ethyl alcohol from ether, 333
Turpentine, absorbent for butadiene, 174
Turpentine, autoxidation of, 905
T.V.P. process, of cracking, 122

U

Ultraviolet absorption, change in, 15
Ultraviolet light, action on acetylene, 266, 703
—, effect on decalin autoxidation, 907
—, — gum formation, 922, 924
—, — nitration of paraffins, 1091
—, — peroxide formation, 922
—, in chlorination of ethane, 741
—, in estimating gum in gasoline, 910
Undecane, from carbon monoxide and hydrogen, 1243
Undecene, in gasoline, 144
—, in kerosene, 145
Undecenoic acid, reaction with hydrogen bromide, 318
—, — hydrogen fluoride, 307
Undecyl ketol, preparation of, 443
Unimolecular law, in cracking of hydrocarbons, 102
Unsaponifiable substances, adsorption by silica, 732
Unsaturates, bromination of, 1150
—, effect of lead tetraethyl on, 1019
—, estimation, by hydrogenation, 1153, 1154
—, —, in gasoline, 1150
—, —, with bromine, 1150, 1152
—, —, with iodine, 1152
—, —, with iodine bromide, 1152
—, —, with iodine chloride, 1152
—, —, with thiocyanogen, 1152, 1153
—, from wax acids, 979
—, reaction with Kattwinkel's reagent, 1150
—, — platinic halides, 628
—, — sulphuric acid, 1150
—, *see also* Olefins
Unsaturation, effect on viscosity, 37
Urania, promoter, esterification of alcohol, 339
Uranic salts, catalyst, oxidation of ethylene, 894
—, —, hydration of acetylene, 712
Uranium, acid salts, catalyst, olefin-carbon monoxide reaction, 626
—. catalyst, reaction of butene with sulphuric acid, 387
—, promoter, oxidation of methyl alcohol, 878
—, —, reduction of carbon monoxide, 1228, 1229, 1230
Uranium boro-phosphate, catalyst, hydration of propene, 292
Uranium chloride, as antiknock, 1018
—. catalyst, polymerization of isobutene, 204
Uranium fluoride, catalyst, cyclization of aliphatic hydrocarbons, 74
Uranium halides, catalyst, dehydrogenation of hydrocarbons, 158
Uranium molybdate, catalyst, oxidation of toluene, 948
Uranium oxide, catalyst, cracking of ethylbenzene, 159
—, —, cyclization of aliphatic hydrocarbons, 74
—, —, dehydration of alcohols, 420
—, —, oxidation of aromatics, 942
—, —, — gas oil, 863
—, —, — kerosene, 966
—, —, — methane, 871
—, —, polymerization of acetylene, 705
—, —, pyrolysis of oxygenated hydrocarbons, 340
—, effect on ignition temperatures, 1000
—, promoter, reduction of carbon monoxide, 1228
Uranium phosphate, catalyst, hydration of ethylene, 284
—, —, — propene, 292
Uranium salts, catalyst, sulphation of propene, 357
Uranium tungstate, catalyst, oxidation of toluene, 948
Uranous-uranic oxide, promoter, reduction of carbon monoxide, 1229
Uranyl oxide, catalyst, cracking of petroleum, 111
Urea, as antiknock, 1018
—, color stabilizer for gasoline, 926
—, in detergents, 1073
—, in fungicides, 569
—, in synthetic plastics, 890
—, reaction with amines, 587
—, — ethylene chlorohydrin, 525
—, — monoethanolamine, 569
Ureides, stabilizers for carbon tetrachloride, 730, 731
Urethans, inhibitors, gum formation, 915
—, preparation of, 569
Useful work, definition of, 1275
Utah wax, oxidation of, 1057
Uvitic acid, from mesitylene, 954

V

Vacuum distillation, effect on corrosive sulphur, 11
Valeric acid, from *n*-amylsulphonic acid, 1067
—, from butylacetylene, 903
—, from paraffin wax, 971
γ-Valero-lactone, solvent for acetylene, 169
Vanadic acid salts, catalyst, hydration of ethylene, 288

Vanadic ions, catalyst, nitration of toluene, 954
Vanadic oxide, catalyst, oxidation of butyl alcohol, 880
—, —, — cracking gas, 881
—, —, — fluorene, 954
—, —, — kerosene, 946, 1047
Vanadium, acid salts, catalyst, olefin-carbon monoxide reaction, 626
—, catalyst, esterification of propene, 307
—, —, hydration of ethylene, 291
—, —, oxidation of ethane, 872
—, —, — methane, 869
—, —, reaction of butene with sulphuric acid, 387
—, in asphalt, 47
—, in asphaltite, 46
—, in lignite, 47
—, in petroleum, 46, 47
—, in shale, 47
—, promoter, oxidation of methyl alcohol, 879
—, use in cracking, 114, 128
Vanadium carbonate, catalyst, oxidation of methane, 881
Vanadium chloride, as antiknock, 1018
Vanadium compounds, effect on stability of lubricants, 938
—, use in acetylene-ammonia reaction, 719
—, — purification of isopropyl alcohol, 365
Vanadium halides, catalyst, dehydrogenation of hydrocarbons, 158
—, —, dichloroethane-hydrogen fluoride reaction, 747
Vanadium oxide, catalyst, cyclization of paraffins, 189
—, —, dehydrogenation of hydroaromatic hydrocarbons, 186
—, —, hydration of acetylene, 713
—, —, hydrogen-carbon reaction, 661
—, —, oxidation of anthracene, 952
—, —, — aromatics, 942, 945, 946, 949, 950
—, —, — gas oil, 863
—, —, — gasoline, 1046
—, —, — hydrogen sulphide, 460
—, —, — methane, 881
—, —, — methyl alcohol, 878
—, effect on ignition temperature, 1000
Vanadium pentoxide, catalyst, oxidation of acenaphthene, 946
—, —, — benzene, 944, 945
—, —, — furfuraldehyde, 945
—, —, — kerosene, 965, 966
—, —, — naphthalene, 946
—, —, — paraffins, 844, 850, 851, 862
—, —, — pentane, 859, 860
—, —, paraffin-nitric oxide reaction, 1091
Vanadium salts, catalyst, sulphation of propene, 357
—, —, oxidation of toluene, 950
Vanadium sulphides, in petroleum, 20
Vanadyl sulphate, catalyst, oxidation of phenylisopropenylcarbinol, 444
Vanillin, for estimation of acetone, 424
Vaporization heat, determination, 1325, 1327
—, —, from boiling point, 1325, 1327
—, —, from characterization factor, 1327
—, —, from molecular weight, 1325, 1327
Vapor-liquid phase cracking, 115
Vapor-phase cracking, 115
—, gases from, 140
—, silent discharge in, 263
Vapor pressure, critical pressure from, 1314, 1315, 1316, 1318
—, of gasoline, determination of, 1169
Vapor-recovery gasoline, octane number of, 1033
Varnishes, preparation of, 728
—, use of asphalts in, 1192
—, use of pentaerythritol esters in, 1055
Varnish remover, preparation of, 790
Varnish resins, preparation of, 1098
Vaseline, fractions of, 40
Vat dyes, ethylenediamine solvent for, 809
Vegetable oil, motor fuel from, 136
Velocity, dissociation of isobutane, 66
—, of cracking reaction, 102
Velocity constant, formation of acetylene from methane, 53
—, — ethylene from methane, 53
Veratryl alcohol, preparation of, 958
Verbenol, from pinene, 905
Verbenone, from pinene, 905
Vinethene, definition of, 529
Vinyl acetate, ethylene oxide from, 553
—, formation of, 717
—, reaction with hydrogen chloride, 718
Vinylacetic acid, reaction with ozone, 902
Vinylacetylene, 1,2-dichlorobutadiene from, 687
—, from acetylene, 680, 704
—, from dichlorobutenes, 685
—, reaction with alkaline hypohalites, 687, 706
—, — alcohol, 705, 706
—, — carboxylic acids, 706
—, — a-chloroethers, 707
—, — Grignard reagents, 708
—, — hydrogen chloride, 680, 706
—, — hydrogen sulphide-sulphur mixture, 709
—, — mercuric salts, 708
—, — potassium mercuri-iodide, 708
—, hydration of, 705
—, polymerization of, 685, 705
—, resin from, 685
—, styrene from, 706
Vinylacetylene acetic ester, polymerization of, 706
Vinyl alcohol, by ethylene oxidation, 896
Vinyl allyl ketone, preparation of, 709
Vinyl bromide, from ethylene dibromide, 504, 505, 533
—, reaction with hydrogen bromide, 315, 716
N-Vinylcarbazole, synthesis of, 719
Vinyl chloride, from acetylene, 716
—, from ethylene dichloride, 496, 497
—, reaction with chlorine, 716
—, — dichloroethane, 811
—, — hydrogen bromide, 315
—, — hydrogen chloride, 716
—, — hydrogen iodide, 716
Vinyl compounds, co-polymerization with chloroprene, 681, 682
Vinylcyclohexane, pyrolysis of, 93
Vinylethinylcarbinols, polymerization of, 708
Vinylethinylmagnesium bromide, reaction with acetone, 708
Vinylethyl sulphide, from acetylene and hydrogen sulphide, 720
N-Vinylindole, synthesis of, 719
Vinyl phenyl sulphide, preparation of, 472
N-Vinylpyrrole, synthesis of, 719
Vinyl radical, from propene, 75, 79
Vinyl resins, from acetylene, 253
Vinyl sulphones, reaction with bisulphites, 618
—, β-sulphoethylsulphones from, 618
Vinyl thioethers, preparation of, 472
Viscosity, characterization factor from, 1309, 1310
—, determination of, 1172-1176
—, effect of polycyclic groups, 37
—, — unsaturation on, 37
—, — silent discharge on, 210
—, of aliphatic hydrocarbons, 37
—, of asphalt, determination of, 1206, 1207
—, —, decreased with phenols, 1218
—, of asphalt emulsions, 1216
—, of crystal oil, effect of ethane, 15
—, —, — butane, 15
—, solutions of paraffins, 15
Viscosity breaking, 116
Viscosity gravity constant, 1176
Viscosity index, characterization factor from, 1309
—, determination of, 1176
—, effect of paraffinic side chain on, 38
Viscosity-temperature stability, of hydrocarbons, 37
Vistanex, definition of, 675
Voltolization, effect of air, 261
—, — hydrogen, 261
—, — nitrogen, 261
—, effect on viscosity, 253
—, of alkylated naphthalenes, 262
—, of aromatics, 261
—, of cracked tar, 262
—, of halogenated paraffins, 262

Voltolization, of hydrogenated tar, 262
—, of kerosene, 261
—, mechanism of, 261
—, of oils, 260-263
—, of olefins, 261
—, of oleic acid, 261
—, of paraffins, 261
—, of stearic acid, 261
Voltol oils, preparation of, 260-263
Volume, reduced, definition of, 1319
Volume-pressure-temperature data, correlation, 1320-1322
Vulcanization, of synthetic rubber, 674

W

Water, antioxidant, paraffin oil, 907
—, azeotropic mixture with isopropyl alcohol, 364, 368
—, carbon monoxide from, 256
—, catalyst, ethylene oxide-aminoacetaldehyde reaction, 561
—, —, styrene-hydrogen chloride reaction, 311
—, effect on asphalt formation in oils, 935
—, — gasoline-alcohol blends, 1035
—, electrical decomposition of, 256
—, estimation in asphalt emulsions, 1221
—, — gasoline, 1168
—, — lubricating oils, 1167, 1168
—, free energy of formation, 1275
—, —, effect of temperature on, 1304
—, hydrogen from, 256
—, in crude petroleum, 10
—, inhibitor, bromination of acetone, 430
—, —, formation of phosgene, 744
—, —, gum formation in gasoline, 909
—, —, olefin formation from isopropyl alcohol, 377
—, use in ethylene oxide-hydrogen sulphide reaction, 564
—, —, oxidation of ethylene, 534, 551, 552
Water gas, carbon monoxide from, 1246
—, ketones from, 268
Waterproofing agents, asphalt emulsions in, 1220
Water vapor, catalyst, bromination of ethylene, 501
—, —, pyrolysis of heptane, 154
—, diluent, carbon monoxide-methyl alcohol reaction, 1050
—, effect on ignition temperatures, 996, 997
Wax, chlorination of, 755, 757
—, chlorinated, reaction with benzene, 758
—, —, — calcium hydroxide, 759
—, —, — diphenylene oxide, 758
—, —, — naphthalene, 817
— — uses of, 758, 759
—, crystallization of, 38
—, effect of precipitating conditions on, 38
—, estimation in asphalt, 1155
—, extraction from asphalt, 1155
—, fractionation in cathode vacuum, 38
—, in ceramics, 1057
—, in paint, 147
—, in petroleum, 13
—, precipitation from oils, 45, 379, 1200, 1201
—, shoemaker's, preparation of, 1058
Wax acids, addition agents for mineral oils, 978, 979
—, aldehydes from, 979
—, as pour point depressants, 979
—, cracking of, 979
—, esterification of, 970, 975
—, from paraffin wax, 970, 971
—, in beeswax substitutes, 970
—, in detergents, 978
—, in emulsifying agents, 978
—, in films, 975
—, in gelatinizing agents, 975
—, in insecticides, 978
—, in lacquers, 975
—, in plastics, 975
—, in soap powders, 978
—, in soaps, 970
—, in softening agents, 975
—, in synthetic fats, 970
—, ketones from, 979
Wax acids, nitriles from, 979
—, pyrones from, 979
—, reaction with ammonia, 979
—, — phenols, 975
—, structure of, 977, 978
—, unsaturates from, 979
Wax alcohols, from paraffin wax, 973
—, properties of, 973
—, refining of, 973
—, use in yeast cultures, 979
Wax distillates, oxidation of, 850
Waxes, crystalline formation, 39
—, nitration of, 1092
—, oxidized, in road bitumen, 1057
—, preparation of, 1056
—, source for petroleum formation, 19
—, specific refraction of, 38
Waxing compositions, carbon tetrachloride in, 731
Wells, drilling of, 8, 9
Wetting agents, alkyl sulphates as, 1085, 1086
—, classification of, 1076
—, diethylene glycol in, 1076
—, ethylene glycol ethers as, 558
—, from aliphatic alcohols, 1076
—, from carboxylic acids, 1076
—, from chlorinated hydrocarbons, 758
—, from mercaptans, 472, 487
—, from oxidized hydrocarbons, 1061
—, from phenols, 1076
—, from tertiary alcohols, 417
—, glycerol in, 1112
—, hydroxyethyl ethers as, 558
—, isopropylnaphthalenesulphonic acid as, 954
—, naphthenic acid salts as, 1117
—, naphthenic acids in, 1112
—, naphthenic alcohols as, 1120
—, sulphonaphthenic acids as, 1118
—, sulphonic acids as, 1075-1077
—, triethanolamine in preparation of, 577, 1076
Wetting properties, of asphalts, 1213
Wild gasoline, butane from, 24
—, propane from, 24
Wood, adsorbent carbon from, 227
—, chlorination of, 227
—, waterproof with asphalt, 1220
Wood flour, use in resins, 625
Wood preservatives, copper naphthenate in, 1115
—, dichlorobenzene in, 790
—, polyglycol arsenites as, 545
Wood rosin, reaction with triethanolamine, 578
Wool, reaction with ethylene oxide, 561
Work content, relation to free energy, 1273

X

Xanthate-iodine titration, of alcohols, 371
Xanthate test, for alcohols, 355
Xenon, effect on acetylene polymerization, 267
X-ray diffraction, of carbon black, 245
—, of paraffin wax, 38
X-rays, action on gaseous hydrocarbons, 267, 268
—, action on water gas, 268
—, estimation of lead tetraethyl with, 1165
—, use, structure of polyethylene oxides, 563
Xylene, action of aluminum chloride on, 208
—, by pyrolysis of ethylene, 182, 186
—, — gas oil, 178
—, — propane, 60, 182
—, demethylation of, 208
—, detection in alcohol, 354
—, extraction agent for naphthenic acids, 1107
—, for dehydration of isopropyl alcohol, 364
—, — *sec*-butyl alcohol, 408
—, for estimation of water in oils, 1168
—, from acetylene and toluene, 719
—, in gasoline, 196
—, reaction with chlorinated Kogasin, 1253, 1254
—, — chloro-*n*-tetradecane, 1254
—, vapor pressure of, 15
m-Xylene, by isomerization of *o*-xylene, 208
—, — *p*-xylene, 208
—, by polymerization of cracking gas, 646
—, by pyrolysis of natural gas, 183
—, — pinene, 88
—, — *p*-xylene, 96

m-Xylene, from toluene, 208
—, hydrogen from, 273
—, in gasolines, 34, 144
—, in shale oil, 35
—, reaction with steam, 273
o-Xylene, by pyrolysis of octane, 73, 74
—, in gasolines, 34, 144
—, isomerization of, 208
p-Xylene, benzene from, 96
—, by polymerization of cracking gas, 646
—, by pyrolysis of cyclooctane, 94
—, — natural gas, 183
—, 2,6-dimethylanthracene from, 96
—, from 2,5-dimethylhexane, 73
—, from toluene, 208
—, in gasoline, 34
—, in motor fuel, 1039
—, isomerization of, 208
—, pyrolysis of, 96
Xylenes, molal entropy, 1289, 1290
Xylenols, antioxidant, for gasoline, 916
Xylidene, antioxidant for gasoline, 917

Y

Yeast cultures, wax alcohols for, 979
Yperite, *see* Dichlorodiethyl sulphide

Z

Zein, refining of, 496
Zeise's salt, *see* Potassium ethylene trichloroplatinate monohydrate
Zeolites, catalysts, decarboxylation of phthalic anhydride, 951
—, —, oxidation of toluene, 949
Zero order reaction, definition of, 501
Zinc, activator, in ethylene oxidation, 553
—, alloys of, use in cracking, 113
—, catalyst, condensation of acetone, 429
—, —, conversion of acetaldehyde to acetone, 423
—, —, — ethylene to butadiene, 172
—, —, dehydrogenation of alcohol, 1051
—, —, oxidation of methane, 881
—, —, — petroleum, 964
—, —, polymerization of olefins, 665
—, —, pyrolysis of alcohol, 350
—, —, — ethylbenzene, 159
—, —, — methane, 158, 257
—, —, rubber compounding, 250
—, effect on chlorinated hydrocarbons, 730, 782
—, inhibitor, deterioration of ethylene oxide, 554
—, nitrocyclohexane reduced by, 1095
—, 2-nitrohexane reduced by, 1094
—, promoter, oxidation of methyl alcohol, 879
—, promoter, reaction of aldehydes and cracked distillates, 625
—, reaction with trichloroethylene, 711
—, use in cracking, 114
—, — dehydrogenation of *sec*-pentanol, 443
—, — preparation of ethers, 715
—, — refining gasoline, 668
Zinc acetate, catalyst, acetylene-acetic acid reaction, 717
—, —, reaction of acetylene and hydrogen sulphide, 472
—, —, — olefin oxides and cellulose, 588
Zinc antimonides, catalysts, dehydrogenation of alcohols, 419
Zinc arsenides, catalysts, dehydrogenation of alcohols, 419
Zinc bismuthates, catalysts, dehydrogenation of alcohols, 419
Zinc bromide, catalyst, esterification of propene, 308, 316
Zinc carbonate, in polymerization of ethylene oxide, 562
Zinc chloride, antioxidant, hydrogenated oils, 914
—, catalyst, alkylation of acid halides, 611
—, —, alkylation of alcohols, 606
—, —, alkylation of phenols, 383, 403, 416, 605
—, —, cracking of oils, 112, 195
—, —, condensation of aldehydes, 886
—, —, dehydrogenation of paraffins, 158
Zinc chloride, catalyst, *p*-dioxane from acetaldehyde, 579
—, —, esterification of olefins, 304, 306, 307, 308
—, —, ether-hydrogen chloride reaction, 345
—, —, ethyl alcohol from ether, 333
—, —, fluorination of carbon tetrachloride, 734
—, —, halogenation of cyclopropane, 761
—, —, hydration of butenes, 294
—, —, — ethylene, 288
—, —, — propene, 292
—, —, hydrogenation of olefins, 670
—, —, isomerization of olefin oxides, 589
—, —, isomerization of paraffins, 72, 202
—, —, polymerization of dichlorobutenes, 685
—, —, — olefins, 195, 636, 640, 641, 642, 646
—, —, — Kogasin, 1255
—, —, preparation of phthalyl chloride, 816
—, —, reaction of alcohols and carbon monoxide, 1050
—, —, — alkyl halides and phenols, 813
—, —, — aromatics and acetylene hydrocarbons, 719
—, —, — olefin oxides and cellulose, 588
—, —, — olefins and chloroethers, 613
—, —, — phthalic anhydride and benzotrichloride, 794
—, —, — phthalic anhydride and thionyl chloride, 945
—, —, — succinic anhydride and thionyl chloride, 945
—, —, vinyl chloride-hydrogen chloride reaction, 716
—, —, voltolization, 262
—, desulphurizing agent, 434, 488
—, for dehydration of hydroxy-acids, 968
—, in aquolysis, 133
—, in dehydration of isopropyl alcohol, 364
—, promoter for activated carbon, 112
—, reaction with ethylene oxide, 560
—, — ethylenediamine, 497
—, —, isopropyl alcohol, 370
—, refining gasoline with, 909, 927-929
—, refining naphthenic acids with, 1109
—, refining of phthalic anhydride, 961
Zinc chloride-aluminum chloride, catalyst, hydration of acetylene, 714
Zinc chromate, catalyst, pyrolysis of alcohol, 352
Zinc chromate-cobalt oxide, catalyst, methane oxidation, 870
Zinc chromite, catalyst, acetone-hydrogen reaction, 432
Zinc compounds, catalyst, acetone synthesis, 714
—, —, acetylene-ammonia reaction, 719
Zinc-copper, catalyst, dehydrogenation of paraffins, 149
Zinc dust, catalyst, formation of *ter*-butyl acetate, 412
Zinc fluoride, catalyst, preparation of propyl fluoride, 307
Zinc fluoride, reaction with carbon tetrachloride, 734
Zinc halides, catalyst, dehydrogenation of hydrocarbons, 158
—, —, dichloroethane-hydrogen fluoride reaction, 747
—, —, hydration of acetylene, 712
—, —, reaction of olefins and carbon monoxide, 625, 626
—, reaction with ketones, 452
Zinc hydrogen phosphate, use in ethylene oxidation, 894
Zinc hydroxide, for hydrogen sulphide removal, 459
Zinc molybdate, catalyst, dehydrogenation of acenaphthene, 955
Zinc naphthenates, as antioxidants, 937
—, as corrosion inhibitors, 1116, 1117
—, as wetting agents, 1117
Zinc oxalate, dehydration of ethylenediamine with, 498
Zinc oxide, catalyst, acetone from acetic acid, 423
—, —, acetone from ethyl alcohol, 421
—, —, acetone-hydrogen reaction, 432
—, —, butadiene from ethyl alcohol, 173

Zinc oxide, catalyst, chlorination of benzene, 781
—, —, cracking of petroleum, 111
—, —, cyclization of aliphatic hydrocarbons, 74
—, —, dehydrogenation of acenaphthene, 955
—, —, — alcohols, 173, 420
—, —, — indenes, 95
—, —, — monoethanolamine, 568
—, — dipropyl ketone from *n*-butanol, 443
—, —, ethyl alcohol from ether, 334
—, —, hydration of acetylene, 712-714
—, —, — ethylene, 290, 191
—, —, hydrolysis of chlorobenzene, 783
—, —, ketones from ethyl alcohol, 423
—, —, olefin oxidation, 553
—, —, oxidation of aromatics, 942
—, —, — *sec*-butyl alcohol, 442
—, —, — methane, 869-871
—, —, — methyl alcohol, 878
—, —, polymerization of ethylene oxide, 562
—, —, — olefins, 665
—, —, preparation of pentaerythritol esters, 1055
—, —, pyrolysis of cyclohexane, 92
—, —, reaction of phthalic anhydride and methyl alcohol, 952
—, —, reduction of carbon monoxide, 1251, 1252
—, —, reforming of gasoline, 189
—, —, rubber compounding, 250
—, effect on ignition temperature, 1000
—, inhibitor, conversion of butene-2 to butadiene, 172
—, reaction with ethylenediamine, 497
—, refining gasoline with, 929
—, promoter, acetone from isopropyl alcohol, 420
—, —, decarboxylation of phthalic anhydride, 951
—, —, methane-steam reaction, 270
—, —, oxidation of acenaphthene, 946
—, —, — naphthalene, 946
—, —, reduction of carbon monoxide, 1228
Zinc oxide-alumina, catalyst, pyrolysis of ethylbenzene, 96
Zinc oxide-chromium oxide, catalyst, pyrolysis of paraffins, 149
Zinc oxide-manganous oxide, catalyst, acetone from acetaldehyde, 714
Zinc phosphate, catalyst, esterification of propene, 308
—, —, hydration of ethylene, 287
Zinc phosphides, catalysts, dehydrogenation of alcohols, 419
Zinc phthalate, benzaldehyde from, 952
—, benzoic acid from, 952
Zinc salts, catalyst, acids from alcohols, 1051
—, —, acetylene-phenol reaction, 715
—, —, ethylacetylene-acetic acid reaction, 718
—, —, hydration of vinylacetylene, 705
—, —, oxidation of hydrogen sulphide, 461
Zinc selenide, catalyst, dehydrogenation of alcohols, 419
—, —, hydration of acetylene, 712
Zinc stearate, catalyst, oxidation of paraffin wax, 971
Zinc sulphate, catalyst, condensation of acetaldehyde, 878
—, —, esterification of propene, 308
—, —, hydration of ethylene, 283
—, —, — propene, 292
—, in desulphurization of oils, 1044
—, in refining gasoline, 670
—, reaction with ethyl alcohol, 878
Zinc sulphide, catalyst, pyrolysis of mercaptans, 472, 479
—, desulphurizing agent, 489
Zinc tellurides, catalysts, dehydrogenation of alcohols, 419
Zirconia, catalyst, dehydration of alcohols, 399
—, —, methane-steam reaction, 272, 278
Zirconium, acid salts, catalyst, olefin-carbon monoxide reaction, 626
—, catalyst, aromatics from olefins, 189
—, —, oxidation of methane, 881
Zirconium carbide, catalyst, oxidation of naphthalene, 946
Zirconium oxide, catalyst, dechlorination of propyl chloride, 805
—, —, dehydration of diols, 548
—, —, hydrolysis of chlorobenzene, 782
—, —, methyl alcohol-carbon monoxide reaction, 1050
—, —, oxidation of aromatics, 942
—, —, preparation of monovinylacetylene, 705
—, promoter, dehydration of alcohols, 420
Zirconium salts, catalyst, oxidation of hydrocarbons, 1051
Zirconium tetrachloride, catalyst, alkylation of aromatics, 200, 596

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